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ANOMALOUS REFLECTIONS IN A SINGLE CRYSTAL NEUTRON SPECTROMETER

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(Communicated by Dr. R. K. Asundi, F.A.SC.)

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Introduction

A single crystal neutron spectrometer is used to produce mono-energetic neutron beams. The diffracted beam in addition to the primary energy also consists of higher orders of energy according to the equation $n\lambda = 2d \sin \theta$.

The experimental values of percentage of higher order neutrons have been compared with the theoretical values (obtained from the reflectivity of the crystals) at a few energies.[1-3] The agreement is never better than 15–20% on account of several uncertain factors. While making an attempt to obtain this comparison at more values of energies it has been noted[4-6] that the curve of neutron counting rate *vs.* Bragg-angle showed fluctuations which were much bigger than the statistical fluctuations. These fluctuations are shown to be a property of the crystal itself. The prominent fluctuations appear to be caused by the double Bragg-reflections by the crystal. Another cause[5] of these fluctuations could be the coherent inelastic scattering by the crystal. In order to check this, theoretical calculations of the differential coherent inelastic scattering cross-section were also made in the case of Al (111) crystal.

Experimental Procedure

In the present measurements, neutrons were obtained through a 10 cm. diameter aluminium tube extending up to the core of Apsara reactor. A steel collimator having in the centre a single slit, 2 mm. wide, 5 cm. high and extending up to 120 cm., was kept at the other end of aluminium tube before the monochromating crystal. The neutron detector, consisting of a 4 cm. diameter enriched BF_3 counter, was moved along the arc of a circle at a distance of 200 cm. from the crystal. An additional 9 cm. long collimator made of aluminium boxes filled with boron carbide having a 5 mm. wide slit was placed in front of the counter. A typical counting rate *vs.* Bragg-angle curve obtained using Al (111) crystal is shown in Fig. 1. In

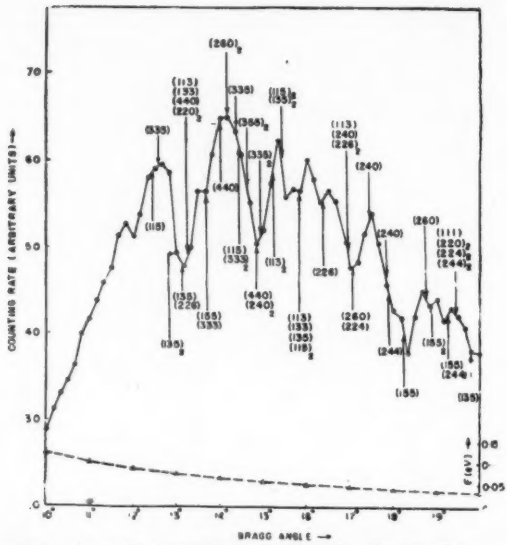

FIG. 1. Counting rate *vs.* Bragg-angle curve of 111 reflection from an Al crystal, plane of reflection being (211). The dotted curve below represents the energies at different Bragg-angles. The position of 1st completing planes (taking part in DBR) is marked. Subscript 2 following the parenthesis indicates the simulation of the primary plane in the 2nd order of reflection.

order to ensure that these fluctuations are not caused by any peculiarities in the incident spectrum from the reactor, the beam hole was surrounded on all sides by 75 cm. of graphite just adjacent to the reactor core. The above curves were repeated with and without a 15 cm. long graphite plug at the end of the beam hole. The fluctuations persisted in each case. The curve in Fig. 1 was obtained without the graphite plug but a $10\times60\times80$ cm.^{3} layer of graphite was introduced between the reactor core and the end of the beam hole. The position and magnitude of the fluctuations were found to be different for different crystals. Thus it was concluded that the fluctuations in the counting rate were caused by the crystal itself.

In order to determine the energy composition of neutrons in the diffracted beam, the percentage of higher order contamination was found[1] by measuring the transmission of two calibrated pyrex plates (absorption cross-section follows $1/v$ law) at all the points. For a given plate,

$$T_{obs} = (1 - A)\,T_1 + aT_2 + bT_3 \qquad (1)$$

where T_{obs} = observed transmission on the crystal spectrometer, T_1, T_2 and T_3 are the calibrated transmissions at the first, second and third order energies respectively.

$A = a + b + \ldots$ = fraction of total higher order contamination.

a = fraction of second order contamination.

b = fraction of third order contamination, etc.

Only the second order fraction was found to be significant. Figure 2 shows

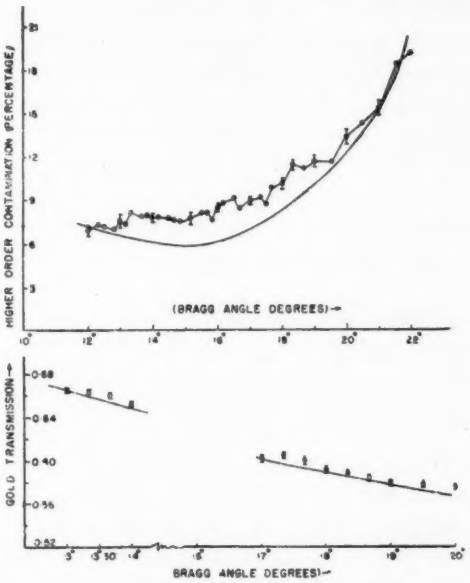

FIG. 2. (*a*) Percentage of higher order contamination *vs.* Bragg-angle of 111 reflection from an Al crystal.—Experimental values obtained with calibrated pyrex plates. Solid curve is obtained from theoretical calculations of reflectivity.

FIG. 2. (*b*) Gold transmission values *vs* Bragg-angle for 111 reflection in Al. Solid lines represent the expected values of transmission, the values of gold cross-section is taken from BNL-325 and the second order contamination values from the theoretical curve of Fig. 2 (*a*).

experimental values of the percentage of higher order contamination at different Bragg-angles. Theoretical calculations of the higher order contamination (represented by the solid line in Fig. 2) were made as follows. In the transmission case, the reflectivity[7] is given by the formula:

$$R^{\theta} = \int_{-\infty}^{+\infty} \sinh(Aa) \exp.\{-A(1+a)\}\, d\Delta \qquad (2)$$

where

$$A = \frac{\mu t}{\cos\theta},$$

$$a = \frac{Q}{2\pi\mu\eta} \cdot \exp.\left\{-\frac{\Delta^2}{2\eta^2}\right\},$$

μ = absorption coefficient of the crystal,

t = thickness of the crystal,

η = mosaic spread of the crystal,

Δ = angle between the normal of a mosaic block and the normal to the crystal surface,

$$Q = \frac{\lambda^3 N^2 F^2}{\sin 2\theta}$$

and

$\lambda = 2d \sin\theta$ = the neutron wavelength,

N = Number of unit cells in 1 c.c.,

F = Structure factor.

The mosaic spread of the crystal was estimated to be 10 min. of arc from the rocking curve of the crystal with and without *a* 0·4 mm. thick C*d* foil before the counter.

Reflectivity R^θ was evaluated from Equation 2 for the first, second and third order enrgies in the case of Al (111) reflection. The integral in Equation 2 was obtained graphically. As the results of reflectivity for Al (111) are not available in literature, these are included in Appendix I.

The percentage of second order neutrons was found out from the relation

$$\frac{\text{Fraction second order}}{\text{Fraction first order}} = \frac{\phi_2(V_2)\, E_2 R_2}{\phi_1(V_1)\, E_1 R_1} \qquad (3)$$

where $\phi_2(V_2)$ and $\phi_1(V_1)$ are the relative fluxes at first and second order energies respectively. Similarly E_1 and E_2 are the counter efficiencies, R_1 and R_2 are the relative reflectivities. The reactor spectrum incident on the crystal was assumed to be of the form:

$$N(E)\, dE = E^{1/2} \exp.\left(-\frac{E}{0{\cdot}025}\right) + 7{\cdot}5 \times 10^{-5} E^{-3/2}\left[1 + \left(\frac{0{\cdot}12}{E}\right)^{16}\right]^{-1}. \qquad (4)$$

The solid curve in Fig. 2 (*a*) represents the theoretical values (after correcting for the insensitive region of the BF_3 counter) of percentage of higher order energy neutrons. The experimental points (plotted as circles)

lie above the theoretical curve. This may be due to the facts that extinction has not been taken into account in the reflectivity formula and the incorrect assumption of the incident neutron spectrum. However the experimental points show fluctuations from a smooth behaviour near 16° and 18°. The reflectivity formula gives a smooth variation and such departures cannot be expected from uncertainty in any of the factors in the reflectivity formula. In Fig. 2 (*b*) are plotted the experimental results of gold transmission at a few angles. Solid lines represent the expected values of transmission (normalised to the experimental points). The values of gold cross-section were taken from BNL-325 and the percentage of the second order energy neutrons was taken from the theoretical values (Fig. 2 *a*). It is seen that the experimental points differ from the expected behaviour.

Comparison with Theory

As a possible cause of these fluctuations, the positions at which double Bragg-reflection (DBR) occur were calculated. This effect in the case of a neutron crystal spectrometer was first pointed out by H. J. Hay[8] and has earlier been observed in X-rays.[9–10] The condition for the occurrence of (DBR) for reflections simulating the forbidden 001 reflections in the case of Be crystal (hexagonal close packed) has been derived by Hay.[8] The underlying idea can be seen from Figs. 3 (*a*) and 3 (*b*) where a reflection in the direction CP occurs for the incident direction CO, if the reciprocal lattice

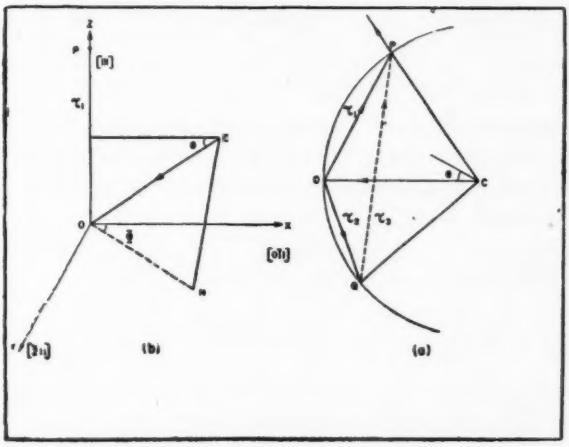

Fig. 3. Diagram of the 'sphere of reflection'.

vector τ_1-terminates at P. A double reflection *via* vectors τ_2 and τ_3 gives a resultant in the same direction and at the same wavelength as a reflection *via* τ_1, whether or not the later is present. Since $\tau_1 = \tau_2 + \tau_3$, the Miller indices of the planes are related by $h_1 = h_2 + h_3$, $k_1 = k_2 + k_3$ and $l_1 = l_2 + l_3$.

In his derivation[8] azimuth angle ϕ has been defined as in Fig. 3 (*b*), where OX, OY and OZ are three mutually perpendicular axes of which OZ is parallel to the vector 001 and OX parallel to the vector 100 in reciprocal space. θ is the Bragg-angle and the angle made by the projection on the $Z = 0$ plane of the radius to the origin (CO) with the X axis is denoted by ϕ.

Following his treatment the condition for the crystal orientation (*i.e.*, primary Bragg-angle θ) at which DBR occurs for simulating the 200 and 111 reflections in the case of cubic crystals has been worked out.

The relations obtained are as follows:

To simulate the 200 reflection,

$$\tan\theta = \frac{2(h\cos\phi + k\sin\phi)}{h^2 + k^2 + l^2 - 2l} \tag{5}$$

and for the 111 reflection

$$\tan\theta = \frac{\sqrt{3}\left[\frac{1}{\sqrt{2}}(h-k)\cos\phi + \frac{1}{\sqrt{6}}(h+k-2l)\sin\phi\right]}{(h^2+k^2+l^2)-(h+k+l)} \tag{6}$$

where *hkl* is the first competing plane and the angle ϕ is defined as in Fig. 3 (*b*) where OZ is taken parallel to vectors [100] and [111] in the above two cases respectively. The vectors taken along two axes are marked in Fig. 3 (*b*) for simulating the 111 reflection.

Figure 4 shows the values of crystal orientation at which DBR occurs to simulate 200 reflection (Eqn. 5) as a function of angle ϕ for a few competing planes. The values obtained for the 111 reflection (Eqn. 6) are given in Appendix II for $\phi = 90°$.

The counting rate curve at different scattering angles obtained from the 200 reflection of KCl crystal [plane of reflection (002)] is shown in Fig. 5. Most of the prominent fluctuations (from the smooth behaviour) can be identified as due to DBR. In the case of the 111 reflection from Al crystal (plane of reflection $(\bar{2}11)$) also, several of the fluctuations can be ascribed to the same effect (Fig. 1). For the Al crystal, the counting rate curves were also obtained for a few values of azimuth angles obtained by rotating the crystal about an axis perpendicular to (111) plane. Figure 6 shows the curve

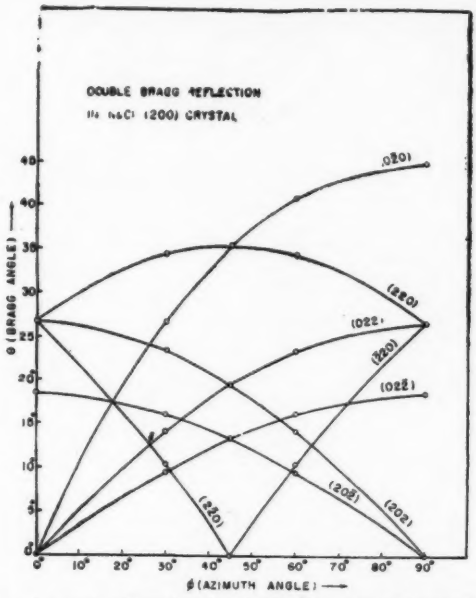

FIG. 4. Curves of crystal orientation for double Bragg-reflections which simulate 200 reflection from NaCl (f.c.c.) *vs.* azimuth angle ϕ (ϕ is defined in Fig. 3).

obtained for $\phi = 5°$. Again the prominent fluctuations can be ascribed to DBR. Similar results were also obtained for $\phi = 10°$ and 20°. With the resolution of the present spectrometer (6′ of arc collimation of the incident beam and about 10′ mosaic spread of the crystal) it is not possible to make a complete study of these fluctuations.

From Figs. 1, 5 and 6 it is seen that almost all the fluctuations are dips —a reduction in the neutron intensity as compared to the neighbouring points. Thus for the crystals studied above, the phenomena of DBR causes mostly depletion of neutron intensity in the diffracted beam. The extinction of the primary beam by the first competing plane is more than the addition caused by the second competing plane taking part in DBR, since the reflectivity of the first competing plane is always larger than the product of the reflectivities of the two competing planes. There is also the additional path travelled by the neutrons in the crystal in order to be reflected by the second competing plane. However a definite increase in neutron intensity would arise, if while using a higher order primary plane, the missing lower order plane gets simulated by DBR. This has been experimentally verified by Hay[8] in the case of the 002 reflection from a beryllium crystal where an

increase in neutron intensity (the extra neutrons having double the wavelength of the Bragg-reflected beam) was observed on account of simulation of missing 001 plane by DBR process. However such a phenomena cannot occur for the case of 200 reflection from KCl crystal where the missing 100 reflection cannot be simulated by DBR process. This is so because, of the two competing planes taking part in DBR to simulate 100, the structure factor of one must always be zero.

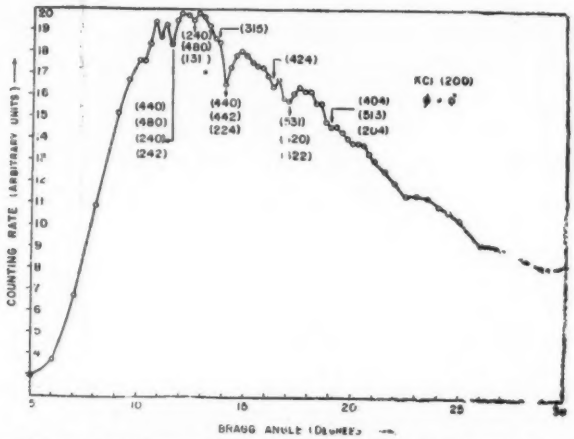

FIG. 5. Counting rate *vs.* Bragg-angle curve obtained from KCl crystal using 200 reflection ϕ (= 0). The position of 1st competing planes (taking part in DBR) is marked.

As the values of crystal orientation at which DBR occurs are in general different for first order and second order energy neutrons, the ratio of the second order to first order energy neutrons in the diffracted beam will be different at these angles. Thus if a change of 20% appears in the counting rate curve, due to simulation of the first order, the ratio of the second order to first order will also change by an equal amount at this angle. However, since in the useful range of the crystal spectrometer this ratio in the diffracted beam is generally less than 10%, a similar change in the value of the ratio can also occur due to simulation of the second order without an appreciable change appearing in the counting rate curve. Thus from the counting rate alone, a correct picture of the change in ratio of the second order to first order cannot be obtained.

In Fig. 2 (*a*), the percentage of the second order energy neutrons (in the diffracted beam) does show fluctuations from a smooth behaviour near 16° and 18°. But corresponding to the big change at 13° in Fig. 1, no marked change appears in Fig. 2 (*a*). The gold transmission results [Fig. 2 (*b*)]

give an idea of the change caused in the transmission results on account of this effect. This change can be rather large if the second order neutron energy lies near a resonance.

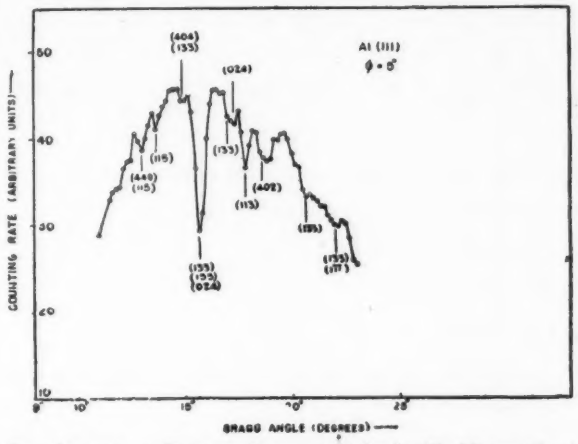

FIG. 6. Counting rate *vs.* Bragg-angle curve obtained with Al crystal using 111 reflection, $\phi = 5°$.

COHERENT INELASTIC SCATTERING

In order to check whether coherent inelastic scattering of neutrons incident on the crystal could cause some of these fluctuations, theoretical calculations were made of the intensity of inelastically scattered neutrons. Only one phonon scattering was considered. The procedure is as follows:

For inelastic scattering to take place, the following energy and momentum conditions are to be satisfied.[11]

$$\mathrm{K} - \mathrm{K}' = 2\pi\tau - q \qquad (7\,a)$$

$$\mathrm{K}'^2 = \mathrm{K}^2 - \epsilon\left(\frac{2m_0}{\hbar}\right) cq \qquad (7\,b)$$

where K and K′ are the incident and outgoing neutron wave vectors. τ is the reciprocal lattice vector of the crystal, where $\epsilon = \pm 1$ depending on whether neutron losses (+) or gains (−) energy in the scattering. The value of C (velocity of sound) was determined from the experimental curves[11] of frequency *vs.* wave-number in aluminium (111) crystal. From Eqn. 7 *b* the value of K′ is found out for each incident wavelength for different values of $q/2\pi$. The Eqns. 7 are then solved graphically for each value of Bragg-ngle to obtain the value of q.

The scattering intensity per unit solid angle and per cell is obtained using the formula as derived by Sjölander.[12]

$$\frac{d\sigma_{coh}}{d\Omega} = \frac{K'}{K} e^{-2W} |F|^2 \frac{\hbar\chi^2}{2M} \frac{(e_\chi c_s)^2}{w_s} \frac{\coth(\beta w_s) + \epsilon}{2} \frac{1}{\left|1 + \epsilon \frac{n \cdot c_s}{v}\right|}$$

$$\chi = K - K', \quad \beta = \frac{\hbar}{2k_B T}, \quad w = \frac{\hbar K'^2}{2m} \quad \text{and} \quad w_0 = \frac{\hbar K^2}{2m}$$

n is the unit vector along scattering direction,

v is the velocity of the scattered neutron,

c_s = group velocity of the wave,

e_χ = unit vector along χ,

$(e_\chi \cdot c_s)^2 = (\sin \theta_2)^2$,

θ_2 is the angle between vectors q and χ. Since the transverse vibrations are taken, sine of the angle is used.

$$\frac{n \cdot c_s}{v} = \frac{nc_s}{v} \cos \theta_1.$$

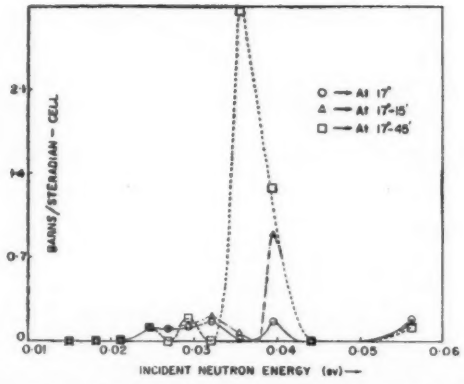

FIG. 7. Theoretical values of coherent inelastic scattering cross-section of Al (111) crystal *vs.* incident neutron energy at 17°, 17° 15′ and 17° 45′.

θ_1 is the angle between q and K′ directions. Using the above formula, the intensity of inelastically scattered neutrons was evaluated at a few Bragg-angles. Figures 7 and 8 show the intensities obtained at 17°, 17° 15′ and 17° 45′ and 23°, 24° 15′, 24° 45′ respectively. These calculations are rather

approximate because of the inaccuracy in the determination of c, q, θ_1 and θ_2. Nevertheless these do show the difference observed at neighbouring angles. The energy of the inelastically scattered neutrons causing the maximum contribution at 17° 45′ is 0·026 ev. whereas the first order Bragg-scattered neutrons are of 0·041 ev. energy. However from the counting rate curve in the case of Al (111) crystal, the effect due to this was found to be extremely small. Only in special cases this could be significant.

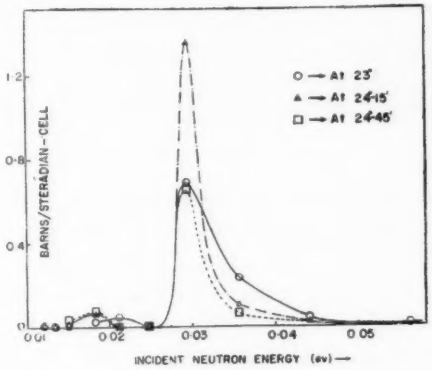

FIG. 8. Theoretical values of coherent inelastic scattering cross-section of Al (111) crystal *vs.* incident neutron energy at 23°, 24° 15′ and 24° 45′.

CONCLUSIONS

The phenomena of double Bragg-reflections can cause fluctuations (peaks or dips) in the neutron counting rate (the diffracted beam) *vs.* Bragg angle curve. In the experiments reported here, most of these fluctuations were found to be dips. These would be more pronounced in crystals having a high reflectivity, a small neutron absorption cross-section and a complex structure. Therefore the reactor spectrum measured with this instrument will be in error since different crystals show characteristic fluctuations.

As the position (and intensity) for the occurrence of DBR differs for diffrent orders, the usual reflectivity relations will not give the correct proportion of higher order energy neutrons wherever DBR is occurring. For measurements of the cross-section of any element, if the second order energy corresponds to a resonance the correction terms can be very serious. It is therefore necessary to measure experimentally the energy composition of the diffracted beam for each crystal used in the spectrometer.

SUMMARY

The counting rate *vs.* Bragg-angle curve obtained with a single crystal neutron spectrometer shows fluctuations. Several of these fluctations are identified as due to double Bragg-reflections by the crystal. The values of differential coherent inelastic scattering cross-section by Al (111) are obtained at a few angles for many incident neutron energies. The effect of this is found to be very small.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. J. N. Soni for his help throughout the course of this work. Thanks are also due to Dr. L. S. Kothari, Dr. V. Padmanabhan and Dr. P. G. Khubchandani for helpful discussions.

Note Added in Proof

Using a chopper and time of flight apparatus, the diffracted beam from a Be crystal has been analysed by R. R. Spencer, J. R. Smith and R. M. Brugger (Symposium on Inelastic Scattering of Neutrons in Solids and Liquids. International Atomic Energy Agency, Vienna, 11–14 October, 1960). It was shown that the ratio of the second order to first order energy neutron flux changes considerably at the dips and these are all due to simulation by the competing plane. No neutrons of other energies (on account of coherent inelastic scattering by Be crystal) were detected.

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APPENDIX I

Relative reflectivities for 111 *reflection from Al crystal (Mosaic spread* $\eta = 10'$*) for 1st, 2nd and 3rd order neutron energies*

Angle (deg.)	$n = 1$ $\times 10^{-3}$	$n = 2$ $\times 10^{-4}$	$n = 3$ $\times 10^{-5}$
5	0·1139	0·1485	0·2919
8	0·3352	0·3840	0·7528
10	0·5221	0·6005	1·1123
12	0·7448	0·8639	1·6667
15	1·1465	1·3419	2·6193
17	1·4369	1·7343	3·4650
20	1·9299	2·4357	4·8934
22	2·2391	2·9732	6·0134
25	2·7055	3·7648	7·9934

APPENDIX II

Bragg-angle at which double Bragg-reflections occur to simulate the 111 *reflection in a face-centred cubic crystal for* $\phi = 90°$ ($n = 1$ *refers to simulation of the* 1*st order and* $n = 2$ *to the* 2*nd order*)

First competing plane	$n = 1$	$n = 2$
111	19° 29′, 54° 44′	29° 30′, 79° 54′
113	10° 2′, 13° 16′, 15° 48′, 16° 52′, 25° 15′, 27° 56′	15° 5′, 26° 32′, 32° 9′, 41° 2′, 59° 30′, 72° 32′
115	3° 41′, 9° 27′, 10° 2′, 12° 28′, 14° 25′, 15° 48′	9° 27′, 15° 25′, 20° 55′, 22° 0′, 23° 31′, 27° 13′, 33° 39′
133	3° 7′, 4° 3′, 6° 43′, 13° 16′, 15° 47′, 21° 27′ 22° 1′	4° 54′, 7° 40′, 11° 2′, 28° 19′, 39° 45′, 48° 32′, 51° 30′
135	5° 30′, 9° 16′, 11° 45′, 12° 35′, 14° 10′, 14° 51′, 15° 22′,	9° 5′, 22° 29′, 23° 11′, 26° 32′, 28° 9′, 30° 20′, 30° 57′
200	25° 14′, 35° 16′	35° 16′, 90°
220	6° 43′, 27° 56′, 35° 16′	10° 2′, 46° 41′, 90°
222	11° 25′, 29° 30′	19° 28′, 54° 44′
240	4° 30′, 9° 16′, 16° 52′, 17° 27′ 17° 49′	10° 2′, 14° 51′, 30° 30′, 35° 16′, 46° 41′
224	2° 54′, 5° 3′, 10° 2′ 11° 25′, 19° 28′	5° 3′, 8° 3′, 19° 28′, 35° 16′, 41° 28′
226	4° 46′, 5° 59′, 7° 40′, 9° 38′, 12° 35′, 13° 49′	10° 1′, 13° 16′, 15° 47′, 16° 52′ 25° 14′ 27° 56′
244	4° 16′, 5° 46′, 6° 13′, 10° 32′, 15° 47′, 16° 14′,	2° 54′, 8° 3′, 10° 1′, 19° 28′, 31° 44′, 35° 16′
333	8° 3′, 19° 28′	14° 25′, 38° 56′
335	3° 0′, 3° 22′, 7° 20′, 8° 23′, 14° 36′, 15° 5′	4° 58′, 6° 5′, 7° 40′, 14° 6′, 14° 56′, 28° 54′ 30° 57′
400	13° 16′, 15° 47′	25° 14′, 35° 16′

ROLE OF SOLVENT IN CHEMICAL REACTIONS

Part IV. Reaction between Bromine and α-β Unsaturated Acids

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Received September 21, 1960

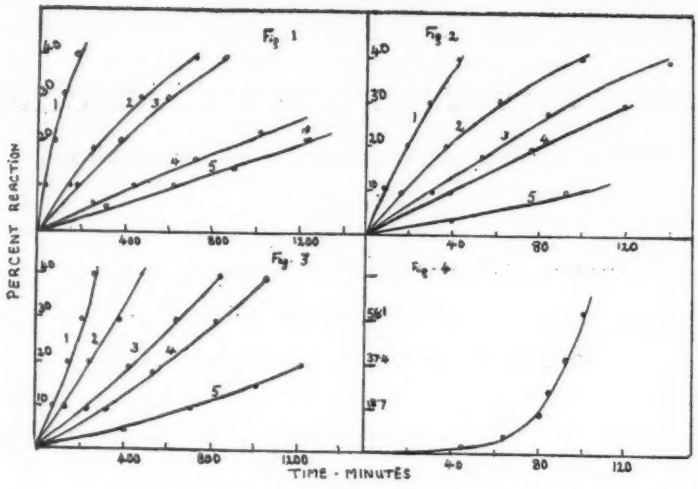
(Communicated by Dr. S. V. Anantakrishnan, F.A.SC.)

Introduction

In earlier parts[5] of this series, the influence of solvents on the alkylation of some amines was examined in both pure and mixed solvents. The systems involved reactants of comparable polarity and a product of an ionic nature and there was inadequate evidence for choosing between a dipole-dipole and ion-dipole rate determining step. Specific solvent effects other than dielectric constant could be better indicated by the solvent mixtures; the observed differences between nitrobenzene and acetone can be partly accounted for by the possibility that the solvation of the transition state by acetone is more effective than by the nitro-compound. Further the need for strictly homogeneous conditions precluded the use of a nonpolar solvent like carbontetrachloride, while in acetic acid the rate was extremely slow. The present studies of a dipole-dipole reaction in which the final product was also of comparable polarity was expected to provide further information in understanding solvent influence. In the thermal addition of bromine to α-β unsaturated acids, the reactants and the products are of comparable polarity and a polar environment is found necessary for a homogeneous reaction.

Experimental

The olefine acids, bromine and the solvents used were purified as in the kinetics of bromine addition[4] and the same technique was followed. Typical experimental results are presented in Figs. 1-4.



FIGS. 1–4.

FIG. 1. Tiglic Acid .. 1. 0·1 M, 80% HOAC
2. 0·1 M, 60% ,,
3. 0·05 M, 80% ,,
4. 0·1 M, 40% ,,
5. 0·025 M, 80% ,,

FIG. 2. ββ-Dimethyl acrylic acid .. 1. 0·05 M, 80% HOAC
2. 0·025 M, 100% ,,
3. 0·05 M, 60% ,,
4. 0·025 M, 80% ,,
5. 0·025 M, 40% ,,

FIG. 3. Transcrotonic Acid .. 1. ·1 M 100% HOAC
2. 90% ,,
3. 80% ,,
4. ·05 M, 100% ,,
5. 80% ,,

FIG. 4. ββ-Dimethyl acrylic acid .. ·025 M in C_6H_5Cl

DISCUSSION

The thermal addition of bromine to α–β unsaturated acids has an induction period, which depends more on the bromine concentration and also varies with the olefine, solvent and temperature. The induction period is less in polar solvents; in solvent mixtures, it increases with an increase in the non-polar component. In highly polar solvents, the induction period may be very small or even absent. The variation of the induction period with solvent

composition can be seen from Fig. 5. The more reactive olefines have a smaller induction period. It was pointed out[1] that the graph of the velocity constant at comparable concentrations, against the induction periods, was a curve asymptotic towards both axes. The induction period decreases with temperature. The behaviour is similar to that of chain reactions, when this period appears to be correlated with the energy of activation of the reaction.[6]

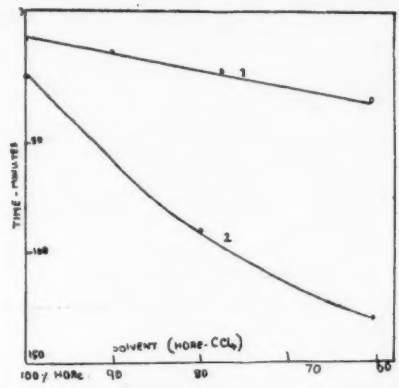


FIG. 5. Induction period and solvent composition:
1. Tiglic Acid .. ·05 M
2. Trans-crotonic acid .. 35° C.

While the reaction in carbon tetrachloride is heterogeneous, an addition of 20% acetic acid by volume, changes the systems to a homogeneous reaction. Preliminary experiments in chlorobenzene with $\beta\beta$-dimethyl acrylic acid (Fig. 4) indicate that the reaction is essentially the same in carbon tetrachloride.

In the thermal addition of bromine to olefines the order of the raction with respect to olefine is unity but the order with respect to bromine varies. The nature of the olefine, the concentration of reactants, the nature of the solvent and in the case of mixed solvents, the composition and probably also temperature, all modify the order with respect to bromine. In $\beta\beta$-dimethyl acrylic acid, the total order seems to be three in pure acetic acid but it increases with carbon tetrachloride content in admixture with acetic acid; tiglic and transcrotonic acids in the concentration range 0·1 M to 0·05 M indicate an "order" 3·5 ! decreasing with an increase in carbon tetrachloride concentration. In the case of transcrotonic acid the order falls to about 2·6 in the concentration range 0·05 M to 0·025 M. But the rate constants calculated

show that no great weight can be attached to the order in the case of a complex reaction like the present one. Transcrotonic acid gives bimolecular constants in ·05 M solutions in carbon tetrachloride. At higher concentrations, however, the rate constants decrease with the progress of the reaction. This may be due to heterogeneous disturbances increasing with dilution and also to the retardation by the products.[3] In carbon tetrachloride for α–β unsaturated sulphones bimolecular constants are reported.[2] The reaction in acetic acid is autocatalytic, this autocatalysis increases with dilution (Fig. 3). The same feature is noticed in the mixed solvents also. The variations in bimolecular rate constants with concentration shown by $\beta\beta$-dimethyl acrylic acid indicates a complex mechanism and even this compound exhibits the characteristic autocatalysis in all the solvents studied, though not to a great extent in pure acetic acid.

TABLE I

Reaction between Olefine acids and Bromine at 35° C. in solvent mixtures (acetic acid—carbon tetrachloride)

Olefine	Conc. of reactions (Olefine = Bromine)	Solvent per cent.	For per cent. reaction			
			100 k_2 Values		k_3 Values	
			10	20	10	20
$\beta\beta$-Dimethyl Acrylic acid ..	0·05 M	80 HOAC	24·15	26·74	24·06	34·39
		60 ,,	7·145	8·306	7·475	10·27
		40 ,,	2·448	2·944	2·632	3·723
	.. 0·025M	100 ,,	26·53	27·93	50·15	58·35
		80 ,,	12·01	13·45	24·16	36·47
		60 ,,	2·931	3·322	5·98	8·491
		40 ,,	0·946	1·149	2·069	2·917
		20 ,,	0·158	0·398	0·554	..
		100 CC14	0·593	1·166	..	..
Tiglic acid ..	0·05 M	100 HOAC	5·420	6·289	..	..
		90 ,,	2·456	2·809	..	..
		80 ,,	1·270	1·356	..	..
		60 ,,	0·389	0·407	..	..
Transcrotonic acid	0·1 M	100 ,,	1·462	1·786	..	..
		90 ,,	0·817	1·008	..	..
		80 ,,	0·439	0·568	..	..
		60 ,,	0·155	0·207	..	..

Neither k_3 nor k_2 values show any constancy. One is forced to conclude that the reaction is a composite one, with both bimolecular and termolecular processes of these, the bimolecular part is more liable to catalysis.

The influence of the catalyst is found to be greater in the nonpolar solvent and the bimolecular contribution becomes greater as the temperature is increased.

The influence of the solvent on the Arrhenius parameters may be seen from the study of allyl compounds (Table II). As the dielectric constant of the medium decreases, the energy of activation as well as the frequency factor decreases in the case of allyl chloride, and 2-methyl allyl chloride. The Arrhenius frequency factor is a measure of the entropy of activation. Decrease in the activation energy is reflected in a more complex, more rigid transition state and hence in a lower entropy. The decrease in the frequency factor due to an increase in the carbon tetrachloride content can be either traced to a reduction in the proportions of the polar acetic acid molecules of the environment or to changes in solvation in the transition state or possibility both.

TABLE II

Arrhenius parameters and solvent composition

Solvent composition per cent.	Allyl chloride (M/80)		2 methyl allyl chloride (M/160)		Allyl proprionate (M/160)	
	E	$\log_{10}PZ$	E	$\log_{10}PZ$	E	$\log_{10}PZ$
100 HOAC ..	2·82	2·94	..	..	..	..
80 „ ..	1·07	1·14	2·68	3·71	7·36	6·88
60 „ ..	1·08	0·55	1·87	2·60	4·69	4·59
40 „ ..	..	..	0·83	1·20	2·74	2·64

For a reaction between dipolar molecules, a linear relationship between $\log k$ and $(D-1)/(2D+1)$ can be expected; this is observed to be followed in the present case (Figs. 6, 7). In solvent mixture, over the concentration range 100% HOAC to 40% HOAC by volume linearity is present, but deviations are distinctly noticed with an increase in carbon tetrachloride content. Microscopic dielectric constant may be different from the bulk value due to segregation of acetic acid molecules and the extent of dimerisation

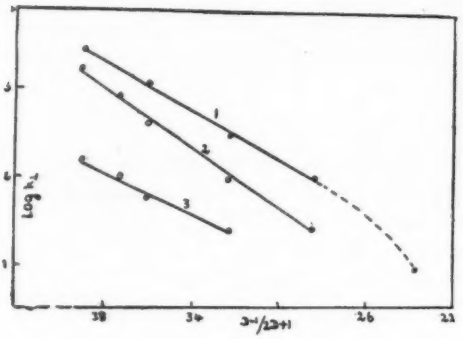


FIG. 6

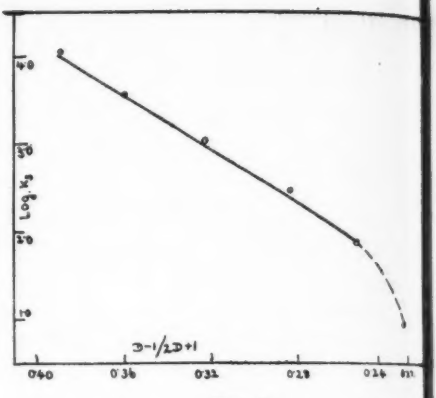


FIG. 7

FIG. 6. $\log k_2$ and $(D-1)/(2D+1)$
$4 + \log k_2$ and $(D-1)/(2D+1)$

FIG. 7. $\log k_2$ and $(D-1/2D+1)$

(1) $\beta\beta$-Dimethyl acrylic acid.
(2) Tiglic acid
(3) Transcrotonic acid
.. Trans stilbene.

of acetic acid can change with the composition of the mixture. Here mention may be made of the observation that these olefine acids react faster in pure carbon tetrachloride than in acetic acid carbon tetrachloride mixture having greater amounts of the inert solvent. The behaviour of polar molecules in "inert" media is complicated by a variety of complex formation. Kinetic studies have to be supplemented by the studies of various physical properties, now in progress. These may give a better picture of the influence of the solvent. The solution is a nonideal one; there is no linear relationship between viscosity and solvent composition nor does the dielectric constant conform to ideal behaviour. Further there is an increase in volume on mixing with attendant heat absorption. For a reaction where the activation energy is low, the chances of a reaction at a given encounter are high and the rate is affected by the diffusion of the molecules through the liquid medium and this a function of the viscosity of the solvent. The viscosity change of the medium is not large enough to make a thorough quantitative study. Further, in solvent mixtures, nonuniformity of the medium may also occur in the vicinity of the reaction zone.

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The author thanks Prof. S. V. Anantakrishnan for his guidance and helpful criticism during the course of this work.

Summary

The reaction between bromine and the α–β olefine acids has been studied in acetic acid carbon tetrachloride mixtures and the influence of the solvent on the reaction has been discussed. The induction period and autocatalysis depend on the nature of the olefine, its concentration and the solvent composition. The change to a more polar medium speeds up the rate, when the charge is generated in the transition state. With an increase in the nonpolar component the frequency factor is found to decrease. A linear relationship between log k_3 and $(D-1)/(2D+1)$ is also noted.

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STUDIES IN OXIDATION : OXIDATION OF SOME AROMATIC SECONDARY ALCOHOLS WITH CHROMIUM (VI) OXIDE—PART II

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(Contribution from the Department of Chemistry, Madras Christian College, Tambaram)

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Introduction

With a view to further elucidating the mechanism of oxidation of secondary alcohols by chromic acid, a series of aromatic secondary alcohols have been investigated in the present studies. The oxidation was carried out as in Part I[18], in binary solvent mixtures of acetic acid and water of several compositions under similarly controlled conditions. The alcohols under investigation were chosen for their structural similarity to isopropyl alcohol, the chromic acid oxidation of which has been studied extensively.[17,18]

Experimental

B.D.H.,-*dl*α–phenyl ethyl alcohol was initially frozen to remove water, subsequently dried over anhydrous magnesium sulfate and then distilled through an effecient column, b.p. 202°. Benzhydrol was prepared by the reduction of benzophenone by zinc and alkali.[8] Fluorenol was prepared in two steps. Fluorene was first oxidised to fluorenone by the method of Schmidt and Wagner[14] and subsequently reduced by zinc dust in alcoholic potassium hydroxide.[16] The other chemicals were purified as detailed in Part I.

The kinetic runs were made at four temperatures between 35° and 50° C. with an ionic strength of 0·4, the pH being kept around 3·5 by an acetate buffer. The unreacted chromic acid was estimated by iodometric titration. Plots of $\log_{10}(a-x)/(b-x)$ against $1/t$ gave good straight lines, indicating that the reaction is of the second order (Fig. 1). The completion of reaction was tested in all cases as before, the alcohols being oxidised to an extent of $\pm 94 \cdot 2\%$.

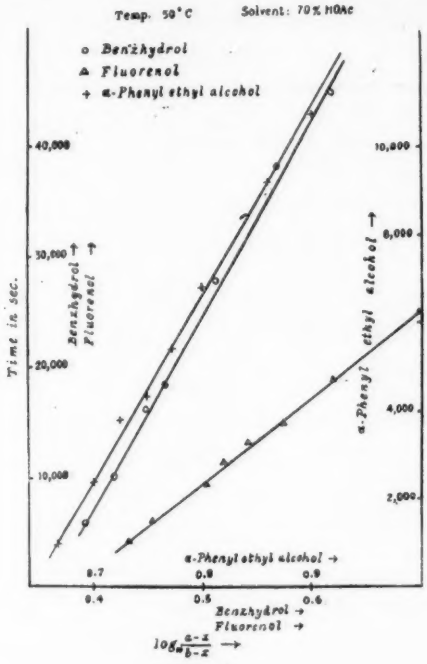

FIG. 1.

RESULTS AND DISCUSSION

The good second order constants (Tables I–III) show that the reaction is of the second order in all cases under conditions of constant pH first with

TABLE I

α–Phenyl ethyl alcohol

(Rates as $k_2 \times 10^4$ 1·mole^{-1} sec.$^{-1}$ and = 0·4 in all cases)

% of acetic acid in solvent mixture	Temperature			
	35°	40°	45°	50°
50	1·676	2·422	3·292	4·842
60	3·313	4·610	6·378	8·913
70	6·922	10·12	13·75	18·49
80	17·58	23·22	32·91	44·55

TABLE II

Benzhydrol

% of acetic acid in solvent mixture	Temperature			
	35°	40°	45°	50°
50	4·266	6·026	8·913	11·75
60	6·200	8·640	12·05	16·63
70	13·34	18·20	26·11	34·12
80	38·02	50·12	70·79	91·20

TABLE III

Fluorenol—9

% of acetic acid in solvent mixture	Temperature			
	35°	40°	45°	50°
50	6·457	9·420	13·03	18·86
60	12·74	17·99	25·14	35·59
70	25·48	38·35	46·61	64·57
80	54·79	76·74	105·95	141·3

respect to the gross concentration of hexavalent chromium and that of the alcohol—a result conforming to the earlier observations with aliphatic secondary alcohols.

Among the three alcohols studied, it is thus seen that *dl*-α-phenyl ethyl alcohol is oxidised slowest and fluorenol-9 is oxidised fastest. The rate of oxidation is slowest in solvent mixtures containing the highest proportion of water.

TEMPERATURE DEPENDENCE OF THE RATE OF OXIDATION

The temperature dependence was determined by plotting $\log_{10}k_2$ or $\log_{10}k_2/T$ against $1/T$ when good linear plots were obtained, the slopes corres-

ponding to the activation energy of the reaction. These and the other derived thermodynamic constants are given below.

TABLE IV

Solvent: 70% *acetic acid*

Alcohol	ΔE (k.cal./mol.)	ΔH (k.cal./mol.)	$\log_1 PZ$	$\Delta S \pm \rho.\mu$
α-phenyl ethyl alcohol	12·85	12·23	5·9781	−31·30
Benzhydrol ..	12·46	11·84	5·9561	−31·45
Fluorenol ..	12·57	11·95	6·3025	−29·84

TABLE V

Added compound	Conc. (M)	$k_2 \times 10^4$	$k_2 \times 10^4$ in absence of compounds
Chromium acetate ..	0·011345	10·798	13·75
	0·00505	11·75	
	0·003001	12·10	
Aluminium acetate ..	0·00505	13·14	
Calcium acetate ..	0·00505	13·02	
Acetophenone (50° C.)	0·03614	18·52	18·49
Pyridine (50° C.) ..	0·01937	18·19	

EFFECTS OF PRODUCTS AND PYRIDINE ON THE OXIDATION

Experiments with added organic products failed to show any change in the rate of oxidation when compared with the rate in absence of any such addition, while the addition of small quantities of chromium acetate, the other product, produced a definite and perceptible retardation of the rate of oxidation as in the aliphatic series. Added aluminium acetate (giving a trivalent cation in solution) and calcium acetate (producing a divalent cation) produced little effect. Hence the observed retardation in the presence of added chromium

acetate is mainly due to the specific prior presence of trivalent chromium ions, the reduction product of hexavalent chromium. Such a specific retardation by added chromium salts and not by other salts has also been noticed earlier in the chromic acid oxidation of formaldehyde and ethylene glycol and substituted toluenes.[6,12] As with isopropyl alcohol, added pyridine, a base, failed to show any perceptible increase in the rate of oxidation. Thus catalysis of the oxidation–an important experimental support to the Westheimer mechanism–could not be confirmed in these experiments also.

It should be pointed out that Roček and Krupička, while investigating the oxidation of isopropyl alcohol in aqueous sulphuric acid solutions, report the absence of any marked effect by added pyridine.

STRUCTURAL INFLUENCES ON THE RATE OF OXIDATION

A comparison of the rate data for the oxidation of the three compounds isopropyl alcohol, phenyl ethyl alcohol and benzhydrol under identical experimental conditions reflects the close structural similarity of these compounds. Table VI brings out the intermediate position occupied by α-phenyl ethyl alcohol in the oxidation, a position justified if one were to trace the difference in the rate of oxidation to the polar influence of the substituents.

TABLE VI

Temperature 40°			$k_2 \times 10^4$
% of acetic acid in solvent	Isopro. oH	Alcohol 1-phenyl Et oH	Benzhydrol
50	0·3905	2·422	6·026
60	0·8353	4·610	8·640
70	1·9030	10·123	18·200

The increased reactivity of α-phenyl ethyl alcohol and benzhydrol over isopropyl alcohol should naturally be traced to the introduction of resonance factors, that are bound to play a prominent part consequent to the introduction of phenyl groups. Moreover, the products, *viz.*, the corresponding resones are much more stabilised relative to the alcohol in the case of the aromatic substances. The same reasoning could be extended to explain the higher reactivity of fluorenol where the resonance stabilisation of the product would

be expected to be higher than in benzophenone, for in this compound the two phenyl groups of necessity should be in the same plane as the carbonyl groups.

A further point of interest is the values for the activation energies for the reactions with α-phenyl ethyl alcohol (12·85–18·49), benzhydrol (12·46–34·12), fluorenol (12·85–64·57) and isopropyl alcohol (12·86–4·37). The first value in bracket is the activation energy in k. cals./mol. and the second represents the second order constant $\times 10^4$. While the rates of oxidation of these alcohols vary considerably it should be surprising that the E values differ but little. This again can be traced to the resonance factors introduced into the aromatic alcohols which is totally absent in the aliphalic alcohols.[4]

Coupled with our earlier observation with the aliphatic secondary alcohols,[18] the foregoing results that increasing amounts of water, the most probable base, actually bring about a decrease in the rate of oxidation, the extra-addition of a base-like pyridine fails to show any catalysis of the oxidation, and the polar influences of substituents on the secondary alochol molecules cannot be easily accounted for by the Westheimer mechanism of ester formation and proton abstraction in the rate-determining step. An alternate way in which the hydrogen can be extracted (since free radicals do not generally appear to be formed as intermediates in the oxidation of secondary alcohols in solution) is the removal of the secondary hydrogen atom as an anion, which could explain the observed sequence of results more convincingly (1 *b*).

For in alkyl compounds the separation of a group with its shared electrons is assisted by the inductive effect of the substituent; and the carbonium ion formed is at best stabilised by hyperconjugative mesomerism. For aralphyl compounds containing an α-phenyl substituent as in α-phenyl ethyl alcohol and benzhydrol, the more powerful mechanism of conjugative electron displacments is available to assist the separation of the displaced group and the carbonium ion formed is stabilised by resonance. That such resonance factors are important in compounds of the benzylic type is well known, *e.g.*, the solvolytic studies on benzyl and benzhydryl halides[7,10] and the bimolecular eliminations from alkyl onium ions. The facilitating polar effect of the α-phenyl substituent in the aromatic secondary alcohols is therefore to be expected.

The concept of hydride ion tranfer to an oxidising agent is by no means unusual and has been previously invoked to explain oxidation reactions[2,5] More recently Roek and Krupička (*loc. cit.*) have offered a cyclic[1] mechanism involving a hydride ion abstraction for the chromic acid oxidation of isopropyl alcohol in sulphuric acid media.

The investigations of the chromic acid oxidation of *p*-substituted α-phenyl ethyl alcohols[11] lend additional support to the hydride abstraction mechanism. These investigations found the following order of reactivities for the *para*-substituents: $CH_3O > \text{tert-}C_4H_9 > CH_3 > H > NO_2$—a result which runs counter to the Westheimer mechanism. The removal of hydrogen as an anion explains the observed order in a simple and straightforward manner, for such removal will become easier as the electron-density in the vicinity of the —CH bond concerned increases as the *para*-substituent becomes more electro-positive. A related experimental finding is the chromic acid oxidation of *para*-substituted toluenes in glacial acetic acid which also shows a dependence of the rate on the electro-negativity of the *para*-substituent.[12]

OXIDATION OF FLUORENOL

This reaction is of special interest in several ways. In the whole series of investigations fluorenol-9 is oxidised fastest in all solvent compositions. It is well known that the 9-position of the fluorene molecule is particularly labile and even the hydrocarbon is readily oxidised in almost quantitative yield to fluorenone by chromic acid in acetic acid.[14] Even though fluorenol can give rise to binuclear oxidation products, under the conditions of the present experiments no indication of the formation of such compounds was noticed. Detailed quantitative crystal analysis has shown that the fluorene molecule has a planar arrangement.[3, 5] The greater oxidation rate of fluorenol over benzhydrol is easily understood when one remembers that the resonance factors (electromeric effect) in fluorenone could be expected to be higher than in benzophenone, because in this compound the two phenyl groups must necessarily be always in the same plane as the carbonyl group. Further the orbitals of π electron system are such that the 9-carbon atom can have a stable charge of either sign. With the proposed mechanism of the oxidation of these compounds, favourable conditions require a stabilised carbonium ion at this position and the rapidity of the oxidation is hence not surprising.

An analysis of the critical increments between benzhydrol and fluorenol reveals, however, certain peculiarities (Table VII).

The difference in Arrhenius activation energies is scarcely outside the limits of experimental error. On the other hand, the frequency factor and the entropy of activation show significant differences. Structural activation of the carbon atom helping the removal of the hydrogen atom as an anion may not be very different when benzhydrol and fluorenol are compared but the longer life of the carbonium ion in the latter leads to a more favourable pre-exponential factor and entropy of activation.

TABLE VII

Solvent 70% acetic acid

Alcohol	ΔE (k.cal./mol.)	$\log_{10} PZ$	$\Delta S^{\pm}$
Benzhydrol ..	12·46	5·9561	− 31·45
Fluorenol ..	12·57	6·3025	− 29·84

SUMMARY

The oxidation of *dl*-α-phenyl ethyl alcohol, benzhydrol and fluorenol by chromium (VI) oxide has been studied in acetic acid-water mixtures under conditions of constant ionic strength and hydrogen-ion concentrations between 35° and 50°. The reaction is of the second order and the rate increases with increasing proportions of acetic acid. The reaction is not a base catalysed one and the results are not explicable on the basis of the hitherto generally accepted mechanism of Westheimer.

ACKNOWLEDGEMENT

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MICROWAVE SPECTRUM OF TRICHLOROACETONITRILE

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Abstract

The microwave spectra of different isotopic species of trichloroacetonitrile—$CCl_3{}^{35}CN$, $CCl_2{}^{35}Cl^{37}CN$, $CCl^{35}Cl_2{}^{37}CN$ and $CCl_3{}^{37}CN$—in the region 20,000–40,100 Mc./sec. have been studied both at room temperature and at low temperature. From the measurements of B_0 values of the symmetric tops, assuming the C–C and C–N bond distances, the other two parameters are determined. They are: C–Cl = 1·771 A, C–C–Cl = 108° 52′.

Introduction

The microwave spectrum of CCl_3CN was reported earlier by Zeil and Pfrommer[1] and by Baker, Jenkins, Kenny and Sugden[2]. Zeil and Pfrommer observed the transition J = 6→7 and 8→9 for the $CCl_3{}^{35}$ CN molecule and calculated the C–C bond distance by assuming the other three parameters. The accuracy of their measurement of the lines was reported to be ± 10 Mc./sec. Baker *et al.*, worked in the region 16,000—27,000 Mc./sec. and reported four lines corresponding to the transitions J = 4→5 to 7→8 of $CCl_3{}^{35}$ CN and also a few lines corresponding to the transition J = 6→7 of the slightly asymmetric top $CCl_2{}^{35}Cl^{37}CN$. The microwave spectra of heavy molecules like CCl_3CN which have low lying vibrational states[3] become complicated as the lines due to the rotational transitions in the excited states will appear with good intensity and also may overlap with the lines in the ground state. As the earlier workers did not consider the possibility of the presence of lines in the excited vibrational states, it appeared that a reinvestigation of the spectrum at room temperature as well as at lower temperature would be necessary to properly identify the lines in the ground state from those in the excited states. The spectrum of other symmetric top

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isotopic species—$CCl_3{}^{37}CN$ was not observed earlier. A determination of the B_0 value of this along with that of $CCl_3{}^{35}CN$ is expected to enable one to determine the molecular parameters more accurately than otherwise. Therefore, a reinvestigation of the microwave spectra of different isotopic species of CCl_3CN was undertaken and the results obtained are reported in this paper.

EXPERIMENTAL METHODS

The sample of CCl_3CN was prepared starting from trichloroacetic acid by the method described by Pierce.[3, 4] It was first distilled under low pressure from the mixture of trichloroamide and phosphorous pentoxide and later fractionally distilled. Before finally using it in the experiments, the sample was further purified by redistillation.

A 100 Kc. Stark Modulation Spectrograph,[5] with a 10½ ft. brass X-band Stark Cell made in the manner described by McAfee, Hughes and Wilson,[6] was used to study the spectra of CCl_3CN. Line frequencies were measured using known appropriate spectral lines as secondary standards, details of measurements being the same as those given elsewhere.[7] The line width and shape were greatly improved by cooling the cell either with freezing mixture or with dry ice. This enables one to distinguish the rotational transitions of the ground state from those of the excited vibrational states.

EXPERIMENTAL RESULTS

The molecule CCl_3CN is a symmetric top having 12 fundamental modes of vibration. The fundamental ν_8 has the frequency 163 cm.$^{-1}$ [3] Therefore, even at room temperature enough molecules can be expected to be in the excited states. At room temperature the lines were quite broad and most

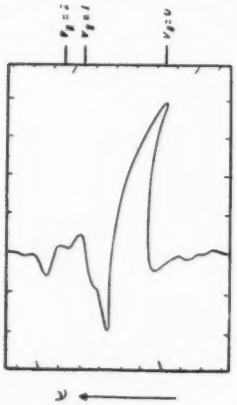

FIG. 1.

of them showed three components, the central one being the most intense. As the cell was cooled, the component on the lower frequency side of the central one became stronger and the one on the higher frequency side became quite weak, sometimes even unobservable. Hence, two of the three lines observed for each transition have been therefore, attributed to the molecules in the excited vibrational states $v_8 = 1$ and $v_8 = 2$. However, when only two components were observed the one on the low frequenccy side became more intense at low temperature and it was therefore taken as belonging to the molecule in the ground vibrational state while the other was taken as belonging to the molecule in the excited state $v_8 = 1$. The recording of the transition $J = 11 \rightarrow 12$ of $CCl_3{}^{35}CN$ showing the lines corresponding to $v_8 = 0$, $v_8 = 1$ and $v_8 = 2$ is shown in Fig. 1. The frequencies of the lines observed for the ground vibrational state are given in Table I while those for the excited states

TABLE I

Frequencies of the observed transitions in the ground state

Isotope	Transition	Frequency Mc./sec.
$CCl_3{}^{35}CN$	5→6	20,009·2
	6→7	23,343·7
	7→8	26,674·5
	8→9	30,009·2
	9→10	33,346·5
	10→11	36,681·9
	11→12	40,050·0*
$CCl_2{}^{35}Cl^{37}CN$	6→7	23,111·9
	7→8	26,394·8
	8→9	29,695·1
	9→10	32,999·9
	10→11	36,301·8
	11→12	39,600·0*
$CCl^{35}Cl_2{}^{37}CN$	7→8	26,115·9
	8→9	29,400·0*
	9→10	32,650·0*
	10→11	35,900·0*
	11→12	39,150·0*
$CCl_3{}^{37}CN$ ..	7→8	25,818·5
	8→9	29,050·0*
	9→10	32,279·5
	10→11	35,499·4

* Frequencies measured with a cavity wavemeter (± 20 Mc./sec.).

are given in Table II. The error involved in the measurements is probably around $\pm$ 1·0 Mc./sec.

TABLE II

Frequencies of the lines observed in the excited states

Isotope	Transition	in $v_8 = 1$ Mc./sec.	in $v_8 = 2$ Mc./sec.
$CCl_3{}^{35}CN$	5→6	20,017·1	20,028·9
	6→7	23,353·2	..
	7→8	26,691·9	26,705·4
	8→9	30,027·4	30,035·0
	9→10	33,363·7	..
	10→11	36,701·7	..
$CCl_2{}^{35}Cl^{37}CN$	6→7	23,127·3	..
	7→8	26,426·0	..
	10→11	36,335·2	..
$CCl^{35}Cl_2{}^{37}CN$ ..	7→8	26,142·3	..

Baker *et al.*,[2] reported lines at 22914, 22992, 23055 and 23138 Mc./sec. and an unresolved group between 23080 and 23120 Mc./sec. which they attributed to sets of different asymmetric top transitions of the molecule $CCl_2{}^{35}Cl^{37}CN$ for $J = 6 \rightarrow 7$. The first four of these were not observed in the present experiments. An unresolved group between 23090 and 23135 Mc./sec. was observed, which is probably the same as the one between 23080 and 23120 Mc./sec. reported by Baker *et al.* This group appeared to have two broad envelopes, each of which probably have a number of unresolved lines. The maxima of these are at 23112 and 23127 Mc./sec. The first one became more intense than the second at low temperature. Similar results were obtained for other transitions of $CCl_2{}^{35}Cl^{37}CN$ and also of $CCl^{35}Cl_2{}^{37}CN$. The envelope having the maximum intensity at low temperature is taken as the one belonging to the molecule in the ground state while the other is taken as the one belonging to the excited state. The results obtained for these molecules are also included in Tables I and II.

The rotational constants B_0 for the molecules $CCl_3{}^{35}CN$ and $CCl_3{}^{37}CN$ have been obtained from the simple equation $\nu = 2B_0(J + 1)$ as the centrifugal stretching constants D_J and D_{JK} can be assumed to be zero since their effect on the spectra could not be observed for the lines measured. The B_0 values are given in Table III.

TABLE III

Rotational Constants and I°_b Values

Isotope	B_0 (obs.) Mc./sec.	B_0 (cal.) Mc./sec.	I°_b (obs.) amu A^2	I°_b (cal.) amu A^2
$CCl_3{}^{35}CN$	$1{,}667{\cdot}3 \pm 0{\cdot}2$	1,667·6	303·17	303·11
$CCl_3{}^{37}CN$	$1{,}613{\cdot}8 \pm 0{\cdot}2$	1,614·1	313·22	313·15

MOLECULAR STRUCTURE

Zeil and Pfrommer,[1] assuming the three parameters C–Cl, C–N and angle C–C–Cl, gave the value of C–C as 1·47 A. Baker *et al.*,[2] with the B value of $CCl_3{}^{35}CN$, the computed values of A,B, C for the $CCl_2{}^{35}Cl^{37}$ and the assumed distance of C–N suggested the structure as C–N = (1·158 A), C–C = 1·46 A, C–Cl = 1·77 A and angle Cl–C–Cl = 109° 56′. The structure had also been determined by thermodynamic[8] and electron diffraction[9] methods.

TABLE IV

Molecular Structure

	C–Cl (A)	C–C–Cl	C–C (A)	C–N (A)	Ref.
This study ..	1·771	108° 52′	(1·46)	(1·158)	..
Zeil *et al.* ..	(1·767)	(110° 24′)*	1·47	(1·158)	1
Baker *et al.* ..	(1·77)	109° 56′*	1·46	(1·158)	2
Janz *et al.* ..	1·761	112°	1·48	(1·158)	8
Rao, C. N. R...	$1{\cdot}76_5$	109° 30′	$1{\cdot}46_5$	$1{\cdot}16_5$	9

* This angle refers to Cl–C–Cl.

The parameters given in brackets are the assumed values.

As only two B_0 values for the symmetric top species were measured and as the asymmetric top lines were not resolved, it was necessary to assume two parameters to determine the complete structure of this molecule. As the isotopic species studied involve only the substitution of chlorine isotopes, it was felt better to assume the bond distances of C–C and C–N to determine the other two—C–Cl and angle C–C–Cl. The C–N bond distance was taken to be 1·158 A, a value obtained in the case of similar molecules,[10, 11] as it is known to be considerably independent of the substitution at the C atom. The C–C distance is assumed to be 1·46 A as in CH_3CN. With these parameters, the other two were calculated and are given in Table IV along with those obtained by earlier workers. The B_0 values calculated for the symmetric tops $CCl_3{}^{35}CN$ and $CCl_3{}^{37}CN$ from these parameters are included in Table III.

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ON TWO-DIMENSIONAL BOUNDARY LAYER IN NON-NEWTONIAN FLUIDS WITH CONSTANT COEFFICIENTS OF VISCOSITY AND CROSS-VISCOSITY

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RECENTLY some papers[1] have come out using the concept of boundary layer in the non-Newtonian flows without actually justifying the boundary layer approximations. In the present note we consider the boundary layer approximations in the two-dimensional flows of the incompressible non-Newtonian fluids with constant coefficient of viscosity μ and constant coefficient of cross-viscosity μ_c. We find that the boundary layer equation reduces to the one of the Newtonian fluid if we suitably replace the pressure p by the modified pressure P defined in the text. With this alterations, the results on two-dimensional boundary layer in Newtonian fluids can be carried over to the non-Newtonian fluids.

2. The equations determining the two-dimensional flow of an incompressible non-Newtonian fluid with constant μ and μ_c are[2]:

Equation of Continuity:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0. \tag{1}$$

Momentum Equations:

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = -\frac{1}{\rho}\frac{\partial p}{\partial x} + \nu\Delta u + \frac{1}{2}\nu_c\left[\frac{\partial}{\partial x}\left\{4\left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}\right)^2\right\}\right] \tag{2}$$

$$\frac{\partial v}{\partial t} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} = -\frac{1}{\rho}\frac{\partial p}{\partial y} + \nu\Delta v + \frac{1}{2}\nu_c\left[\frac{\partial}{\partial y}\left\{4\left(\frac{\partial v}{\partial y}\right)^2 + \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}\right)^2\right\}\right]. \tag{3}$$

We shall now measure x along the length of a flat plate which is also the direction of the flow at infinity, and y along the normal to the plate.

As usual we assume

$$u,\ \frac{\partial u}{\partial x},\ \frac{\partial^2 u}{\partial x^2},\ \frac{\partial p}{\partial x}$$

of the standard order and y of the order δ. Then from the equation of continuity, we find

$$v = 0(\delta). \tag{4}$$

Also, if the viscosity and cross-viscosity have to play a role in shaping the flow, we find from (2) that

$$\nu = 0(\delta^2) \text{ and } \nu_c = 0(\delta^2) \tag{5}$$

and then the equation (2) may be written as

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = -\frac{1}{\rho}\frac{\partial p}{\partial x} + \nu\frac{\partial^2 u}{\partial y^2} + \frac{1}{2}\nu_c\frac{\partial}{\partial x}\left(\frac{\partial u}{\partial y}\right)^2 + 0(\delta)$$

$$= -\frac{1}{\rho}\frac{\partial}{\partial x}\mathrm{P} + \nu\frac{\partial^2 u}{\partial y^2} + 0(\delta), \tag{6}$$

where

$$\mathrm{P} = p - \frac{1}{2}\mu_c\left(\frac{\partial u}{\partial y}\right)^2. \tag{7}$$

A similar consideration of order in equation (3) gives us

$$-\frac{1}{\rho}\frac{\partial p}{\partial y} + \frac{1}{2}\nu_c\frac{\partial}{\partial y}\left(\frac{\partial u}{\partial y}\right)^2 = 0(\delta) \tag{8}$$

or

$$\frac{1}{\rho}\frac{\partial \mathrm{P}}{\partial y} = 0(\delta). \tag{9}$$

Thus we find that to our approximation, P (and not p as usual in Newtonian fluids) does not vary with y across the boundary layer.

Further, since at the edge of the boundary layer $\partial u/\partial y = 0$,

$$\mathrm{P} = p - \frac{1}{2}\rho\nu_c\left(\frac{\partial u}{\partial y}\right)^2 = p_0, \tag{10}$$

where p_0 is the corresponding pressure in the potential flow. Hence we may write the equation (6) in boundary layer approximation as

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = -\frac{1}{\rho}\frac{\partial p_0}{\partial x} + \nu\frac{\partial^2 u}{\partial y^2} \tag{11}$$

and then the pressure in the boundary layer is given by

$$p = p_0 + \frac{1}{2}\rho\, \nu_c \left(\frac{\partial u}{\partial y}\right)^2. \tag{12}$$

From (12) we conclude that the pressure in the non-Newtonian boundary layer has to be more than in the corresponding boundary layer of the Newtonian fluid with the same coefficient of viscosity by the amount $\frac{1}{2}\mu_c\,(\partial u/\partial y)^2$ which decreases from $\frac{1}{2}\mu_c/\mu^2\,\tau_w{}^2$ on the wall to 0 at the edge of the boundary layer. The value of p_0 as usual is determined by the equation

$$\frac{\partial U}{\partial t} + U\frac{\partial U}{\partial x} = -\frac{1}{\rho}\frac{\partial p_0}{\partial x}. \tag{13}$$

In the case of the steady flow, the boundary layer equations are:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0$$

$$u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = U\frac{\partial U}{\partial x} + \nu\frac{\partial^2 u}{\partial y^2} \tag{14}$$

where the pressure in the boundary layer is given by

$$p = p_{0\infty} + \frac{1}{2}\rho\,(U_\infty{}^2 - U^2) + \frac{1}{2}\mu_c\left(\frac{\partial u}{\partial y}\right)^2. \tag{15}$$

3. From the above discussion, we conclude that the velocity distribution in the case of the present class of non-Newtonian fluids is the same as in the Newtonian fluids with the same coefficient of viscosity μ. However, the cross-viscosity exhibits itself through the increase in pressure at each point of the boundary layer.

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CHEMICAL EXAMINATION OF THE LEAVES OF *RHODODENDRON CAMPANULATUM* D.DON.

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Plants belonging to the genus *Rhododendron* are considered to be poisonous to cattle.[1] The results of the chemical examination of the leaves of *Rhododendron falconeri* Hook. and the leaves and flowers of *Rhododendron nilagiricum* Zenk. have been reported in earlier communications from these laboratories.[2–4] *Rhododendron campanulatum* D.Don. is an evergreen gregarious shrub and is found in the outer and inner ranges of the Alpine Himalayas from Kashmir to Bhutan at altitudes of 9,000 to 14,000 ft. The leaves of the plant are said to possess several medicinal and poisonous properties.[1, 5, 6] There is only a single reference recorded in the literature to past chemical work on this species.[7] It is stated therein that a specimen of the leaves, obtained from Kashmir, was analysed and a toxic substance was isolated, whose chemical and pharmacological properties resembled those of andromedotoxin. The results of a systematic chemcial examination of the leaves of this plant are described in the present paper.

The dried leaf powder was extracted successively with petroleum ether, ether and methanol. From the petroleum ether extract, by suitable manipulation as described in the experimental section, a new substance designated as "campanulin", epifriedelanol, minor component 1, m.p. 74–76°, and minor component 2, m.p. 168–70°, were obtained. The ether extract, on complete removal of the solvent, gave a dark green residue from which the colouring matter was removed by treating with petroleum ether and acetone. The acetone-insoluble residue, by fractional crystallization and chemical separation, could be separated into ursolic acid and minor components 3 and 4 having melting points 248–52° and 272–74°, respectively. Concentration of the methanol extract deposited greenish solids from which ursolic acid was again obtained. The mother liquor, on acid hydrolysis, gave quercetin.

We consider campanulin to be a new triterpenoid compound. Its chemical constitution will be discussed in a separate communication. The minor component, m.p. 198°, obtained from the leaves of *Rhododendron falconeri* Hook. (*see* p. 246 in ref. 2) has now been found to be identical with campanulin.

The identity of epifriedelanol obtained in the present investigation was deduced from the colour reactions, melting points, mixed melting points, optical rotations and analyses of the parent compound and its benzoate.

Ursolic acid and quercetin were identified through their properties and those of their acetates and by mixed melting points.

Experimental

The material was obtained from Darjeeling, N. India. The coarsely powdered leaf (3 kg.) was extracted with petroleum ether (4×12 l.) in the cold, then with ether (4×13 l.) in the cold and finally with methanol (3×12 l.) under reflux.

Petroleum ether extract.—The united dark green extract, on concentration to about 250 ml. and leaving at room temperature for a number of days, deposited a good amount of crystalline material. This was filtered and washed with warm acetone till the washings were only slightly coloured (fraction 1, 4·1 g.). The filtrate was concentrated to a low volume and seeded with fraction 1 obtained above. On keeping aside for a day, a further quantity of crystalline material separated along with some waxy matter. As the solid could not be filtered under suction, the mixture was vigorously shaken with petroleum ether (50 ml.) when the waxy portion went into solution. The residual crystalline portion was filtered and washed with petroleum ether (fraction 2, 4·8 g.). The filtrate, on complete removal of the solvent, gave a dark green sticky residue (residue X, 90 g. *see* later).

Fraction 1.—This was found to be a mixture of long prismatic rods and short cubes, which were separated mechanically. Recrystallization of the former (rods) twice from benzene-petroleum ether yielded colourless needles, m.p. 204° (campanulin, 2·3 g.).

When the m.p. of the other crystalline portion (cubes) (1·5 g.) was taken on a Kofler block, a trace of the residue melted at 195°, but the major portion melted only at 270–74°. The crystals were dissolved in excess of hot chloroform, filtered and the filtrate was concentrated to a low volume and left aside. A heavy crystalline substance (plates, *see* below) deposited slowly. The turbid supernatant liquid was decanted, heated to get a clear solution, concentrated and set aside, when a small quantity of a crystalline powder separated. This was filtered and crystallized twice from chloroform-acetone when colourless nodules were obtained, m.p. 74–76° (minor component 1, 30 mg.). The mother liquor, on removal of the solvent, gave a residue which was crystallized from benzene-petroleum ether when colourless needles were obtained, m.p. 201–03° (0·3 g.). It was found to be identical with campanulin.

The heavy deposit of plates mentioned above, was crystallized twice from chloroform when glistening colourless plates were obtained, m.p. 281–82°. Further crystallizations from benzene did not improve the m.p. (epifriedelanol, 0·8 g.).

Minor component 1 was insoluble in cold acetone and only sparingly soluble in cold chloroform. No colour was obtained either in the Salkowski or in the Liebermann-Burchard test. Owing to insufficiency of the material it could not be examined further.

Fraction 2.—Crystallization of this fraction twice from benzene-petroleum ether yielded colourless needles, m.p. 200–02° (3·9 g.). This was also found to be identical with campanulin (mixed m.p. and colour reactions).

Campanulin.—The substance was almost insoluble in acetone, methanol and cold glacial acetic acid, sparingly soluble in pyridine, alcohol and hot glacial acetic acid, moderately soluble in benzene and petroleum ether and readily soluble in cold chloroform. In the Salkowski reaction the yellow colour immediately formed gradually changed to orange-yellow. In the Liebermann-Burchard test an immediate deep red colour was obtained which rapidly turned deep pink. In the Tschugaeff reaction, an immediate yellow colour was obtained. On warming the reaction mixture, the colour changed to orange-red and then to blood-red in about three minutes. A deep red colour was obtained when the substance was warmed with trichloroacetic acid; the solution exhibited a bright yellow fluorescence under U.V. light (Hirschsohn reaction[8]). $[\alpha]_D^{29} = +75{\cdot}2° \pm 2°$ ($c = 1{\cdot}085$ in chloroform). [Found: C, 84·8; H, 11·4. $C_{30}H_{50}O$ (probable formula of campanulin) requires: C, 84·5; H, 11·8%.]

Epifriedelanol.—The substance gave a yellow colour in the Salkowski reaction. In the Liebermann-Burchard test a red colour changing to deep pink was obtained. No colour was obtained with tetranitromethane in chloroform. $[\alpha]_D^{29} = +25{\cdot}6° \pm 3°$ ($c = 0{\cdot}978$ in chloroform). [Found: C, 84·2; H, 12·6. $C_{30}H_{52}O$ (epifriedelanol) requires: C, 84·1; H, 12·2%.) Mixed m.p. with an authentic sample of epifriedelanol, isolated from the leaves of *R. nilagiricum* Zenk.,[3] was undepressed.

The benzoate, prepared by heating the substance (0·15 g.) with pyridine (5 ml.) and benzoyl chloride (1 ml.) at 110° for 4 hours and working up in the usual way, crystallized from benzene-alcohol as shining colourless plates, m.p. 250–52°. $[\alpha]_D^{29} = +31{\cdot}3° \pm 4°$ ($c = 0{\cdot}748$ in chloroform). [Found: C, 83·9; H, 10·9. $C_{37}H_{56}O_2$ (epifriedelanol benzoate) requires: C, 83·4; H, 10·6%.] Mixed m.p. with an authentic sample of epifriedelanol benzoate[3] was undepressed.

Residue X (*see* para 2 of experimental).—This was saponified with 1 N alcoholic potash and the unsaponifiable matter was extracted in the usual way. It was dissolved in petroleum ether and set aside for a number of days when a minute quantity of a crystalline residue was obtained which was filtered. Recrystallization twice from petroleum ether yielded colourless needles, m.p. 168–70° (10 mg. minor component 2). This was not examined further.

Ether extract.—The extract, on complete removal of the solvent, gave a dark green syrupy residue (*ca.* 65 g.). It was boiled under reflux with petroleum ether (3×1 l.) and the extracts were filtered. The united dark green extract was concentrated to a low volume (200 ml.) and left in the ice-chest for a number of days. As no crystalline material deposited, it was not examined further.

The petroleum ether-insoluble residue still contained a considerable amount of the colouring matter. It was triturated with acetone (4×500 ml.) when the colouring matter went into solution. The suspension was filtered and the residue washed with acetone till the washings were only slightly coloured. Evaporation of the filtrate yielded a greenish sticky residue (25 g.) which was also not examined further.

The light green acetone-insoluble residue was dissolved in excess of benzene-methanol (1 : 1, 300 ml.) and filtered through a thin bed of charcoal. The clear filtrate, on partial removal of the solvents and allowing to stand, deposited colourless plates, m.p. 270–74° (fraction 3, 12·5 g.).

The mother liquor of fraction 3 was evaporated to a syrupy residue (8·2 g.). This was dissolved in hot benzene-methanol (1 : 1, 200 ml.), cooled and diluted with water (100 ml.) when two layers separated. The lower aqueous methanol layer (suspension) was tapped into another separating funnel, extracted with ether (4×200 ml.) and the ether extracts were united with the benzene phase. The resulting benzene-ether solution (900 ml.) was shaken with 5% sodium hydroxide solution (4×100 ml.) when a precipitate separated at the interphase. This was filtered from the alkaline layer and washed with water. The precipitate, the alkaline filtrate and the solvent layer were worked up separately as described below.

The precipitate was dissolved in methanol (100 ml.) and the solution was acidified with hydrochloric acid (1 : 1) to congo red when a colourless precipitate separated out. The resulting suspension was concentrated to 50 ml. and left in the ice-chest for a day. The solid that separated was filtered and washed with water (fraction 4, m.p. 278–80°, 6 g.).

The alkaline filtrate yielded only a small quantity (0·2 g.) of an amorphous residue on acidification and extraction with ether; it was not examined further.

The benzene-ether solution was washed neutral and dried and the solvents were removed when a waxy residue (0·95 g.) was obtained. This was chromatographed over alumina (30 g.). The waxy solid obtained from the initial petroleum ether eluate was treated with warm benzene when the waxy portion went into solution leaving behind a small quantity of a crystalline residue. Recrystallization from benzene-petroleum ether yielded colourless needles, m.p. 248–52° (10 mg., minor component 3). The residues obtained from the subsequent petroleum ether-benzene (9:1, 4:1 and 1:1) eluates were separately crystallized from benzene-petroleum ether. As the crystalline substances all melted between 268–74°, they were united and recrystallized from benzene-petroleum ether when colourless prisms were obtained, m.p. 272–74° (20 mg., minor component 4). Minor components 3 and 4 both gave a light yellow colour in the Salkowski reaction and a pink colour in the Liebermann-Burchard test.

Fractions 3 *and* 4.—As these two fractions gave identical colour reactions, they were united and crystallized from excess of alcohol when colourless needles were obtained, m.p. 282–83°. $[\alpha]_D^{29} = +66{\cdot}6° \pm 2°$ ($c = 1{\cdot}216$ in absolute alcohol). [Found: C, 78·5; H, 11·1. $C_{30}H_{48}O_3$ (ursolic acid) requires: C, 78·9; H, 10·6.%] In the Liebermann-Burchard test it gave a red colour, changing to violet, then to blue and finally to green. Mixed m.p. with an authentic sample of ursolic acid from *R. falconeri* Hook.[2] was undepressed.

The acetate crystallized from alcohol as colourless needles, m.p. 282–84°. $[\alpha]_D^{29} = +67{\cdot}8° \pm 3°$ ($c = 1{\cdot}127$ in chloroform). [Found: C, 77·5; H, 10·6. $C_{32}H_{50}O_4$ (ursolic acid acetate) requires: C, 77·1; H, 10·1%.] Mixed m.p. with an authentic sample of ursolic acid acetate[2] was undepressed.

Methanol extract.—The united extract (36 l.) was concentrated to about 1·5 l. and left overnight at room temperature when a greenish granular solid deposited (fraction 5, 10 g.) which was filtered. Further concentration of the filtrate to about 700 ml. deposited some more greenish solid (fraction 6, 4·8 g.) and a sticky mass (2 g.) which were collected separately. The final filtrate gave a weak but positive test for anthoxanthins. It was hydrolysed by adding concentrated sulphuric acid to give a 7% strength and refluxing the mixture for 2 hours. The hydrolysate was diluted with water (250 ml.), the alcohol was removed by distillation and the resulting brown suspension was extracted with ether (4×200 ml.). The united ethereal extract was washed

with water till neutral, dried and the solvent removed. Repeated crystallization of the reddish-yellow residue from dilute alcohol yielded fine yellow needles, m.p. 306–10° (decomp.) (0·2 g.). The substance gave a scarlet-red colour with magnesium and hydrochloric acid and an orange precipitate with neutral lead acetate solution. It gave a green colour with alcoholic ferric chloride [Found: C, 59·4; H, 3·7. $C_{15}H_{10}O_7$ (quercetin) requires: C, 59·6; H, 3·3%). The acetate crystallized from alcohol as colourless needles, m.p. 197–98°. [Found: C, 58·4; H, 4·2. $C_{25}H_{20}O_{12}$ (quercetin penta-acetate) requires: C, 58·6; H, 3·9%.] Mixed m.p. with an authentic sample of quercetin penta-acetate[2] was undepressed.

Fractions 5 *and* 6.—These were united and triturated with acetone (100 ml.) when much of it including the colouring matter went into soloution. The undissolved portion was filtered, washed with acetone and crystallized from methanol-benzene and then from alcohol when colourless needles were obtained, m.p. 280–82° (3 g.). It answered the colour reactions of ursolic acid $[\alpha]_D^{29} = +66{\cdot}9° \pm 2°$ ($c = 0{\cdot}942$ in absolute alcohol). The acetate crystallized from alcohol as colourless needles, m.p. 282–84°. $[\alpha]_D^{29} = +64{\cdot}9° \pm 3°$ ($c = 1{\cdot}204$ in chloroform). Mixed melting points of the acid and its acetate with the respective authentic samples were undepressed.

Summary

The chemical examination of the leaves of *Rhododendron campanulatum* D.Don. by extraction with solvents is described. Besides ursolic acid, quercetin and the saturated triterpenoid alcohol epifriedelanol, a new triterpenoid compound, designated as " campanulin ", has been isolated in reasonable yields. A few minor components have also been obtained.

Acknowledgments

We thank Dr. V. S. Rao, Conservator-General of Forests, West Bengal, and Mr. D. K. Dey, Divisional Forest Officer, Darjeeling Division, West Bengal, for supplying the material used in this investigation. We thank Mr. R. V. Krishna Rao for the microanalyses. We also thank the Council of Scientific and Industrial Research for financial assistance.

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RAMAN SPECTRA OF ADDITION COMPOUNDS OF GLYCINE (DIGLYCINE HYDROCHLORIDE, DIGLYCINE HYDROBROMIDE AND DIGLYCINE NITRATE)

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1. Introduction

In two papers which appeared in these *Proceedings*, Krishnan and Balasubramanyam (1958 *a*, *b*) reported the results obtained from a study of the Raman spectra of single crystals of α-glycine (G) and triglycine sulphate (G_3S). In continuation of this work, the Raman spectra of single cystals of three more addition compounds of glycine, namely, diglycine hydrochloride (G_2Cl), diglycine hydrobromide (G_2Br) and diglycine nitrate (G_2N) have been investigated and the results are presented here. These substances will hereafter be referred to by their respective shorter symbols as indicated in the brackets. The Raman effect in these substances has not been investigated so far. As they are transparent to the ultraviolet, the λ 2536·5 resonance radiation of mercury was used as exciter.

2. Experimental

Fairly large, transparent crystals of G_2Cl, G_2Br and G_2N were grown by slow evaporation of aqueous solutions of the constituents in stoichiometric proportions. The molecular formulæ of these crystals were established from density as well as X-ray measurements. Well-developed crystals were in the form of parallelepipeds of 2 cm. $\times \frac{1}{2}$ cm. $\times \frac{1}{2}$ cm. in the case of G_2Cl and G_2Br and 1 cm. $\times \frac{1}{2}$ mm. $\times \frac{1}{2}$ mm. in the case of G_2N. The diglycine hydrohalides grow along the *c*-axis. The spectra were taken using a Hilger medium quartz spectrograph with 0·003 cm. slit width. Exposures of the order of 5 to 6 hours were found to be sufficient to get intense spectrograms using λ 2536·5 excitation. In the case of G_2Cl the scattering was taken at along the *c*-axis and the illumination was approximately 45° to the *b*-axis. In the case of G_2Br the *c*-axis was placed perpendicular to the plane of incidence and scattering. Scattered light along the *b*-axis was photographed in the case

of G_2N. The faces of G_2N used to get frosted due to exposure to the ultraviolet radiation and the crystal specimen had to be polished frequently. Frequency shifts of the very faint lines have been estimated from the microphotometer records.

3. RESULTS

Enlarged photographs of the Raman spectrum of single cystals of G_2Cl, G_2Br and G_2N together with their respective microphotometer records are reproduced in Figs. 1 to 3 in the accompanying plate. For the purpose of comparison the mercury arc spectrum in the ultraviolet region is also included. The principal Raman lines are marked in the microphotometer records. The frequency shifts have been listed in Tables I and II. The frequency shifts observed by the author in triglycine sulphate, and α-glycine are given in columns 5 and 6 respectively in Tables I and II.

TABLE I

Internal frequencies

Sl. No.	Diglycine hydrochloride	Diglycine hydrobromide	Diglycine nitrate	Triglycine sulphate	α—Glycine	Assignment
1	330 (2 *d*)	330 (3 *d*)	311 (1 *d*)	330 (6 *d*)		C–C
2	354 (6)	354 (6)	349 (3)	345 (2)	358 (35)	Torsion
				450 (10)		$SO_4^{--}-\nu_2$
				463 (6)		
3	504 (8)	504 (5)	505 (6)	500 (6)	499 (5 *bd*)	$-COO^-$ rocking
	518 (7)	518 (7)				
			540 (2)			O–NO_2
			561 (2)			
	575 (4)	571 (4)				
4	587 (3)	584 (3)		587 (3 *d*)	588 (1)	$^-COO^-$ Wagging
				610		$^-SO_4-^-\nu_3$
				629 (6 *d*)		
5	665 (3 *bd*)	660 (2 *d*)	689 (3)	665 (6 *d*)	677 (1)	$-COO^-$ bending
				697 (3)	697 (3 *d*)	
6	878 (18)	873 (13)	869 (4)	870 (10)		$-COOH$?
7	890 (12)	889 (8 *b*)	898 (10)	890 (12)	896 (8 *b*)	CCN stretch
8	914 (8)	913 (3)	924 (4)	902 (8)	925 (3)	OH out of plane bend ?
				980 (20)		$-SO^{--}-\nu_1$
				1009		
9	1036 (8)	1034 (10)	1053 (5)	1040 (6 *d*)	1038 (3 *s*)	CCN stretch
				1092 (3 *d*)		$SO_4^{--}-\nu_4$
				1104 (6)		

TABLE I (*Contd.*)

Sl. No.	Diglycine hydrochloride	Diglycine hydrobromide	Diglycine nitrate	Triglycine sulphate	α-Glycine	Assignment
10	1106 (10)	1104 (12)	1132 (5)	1114 (8)	1112 (2*s*)	
11	1132 (12)	1124 (10)	1144 (3)	1134 (8)	1140 (3*s*)	NH_3^+ rocking
				1164 (4 *d*)		
	1249	1248				C–OH ?
	1267 (5 *d*)	1264 (3 *d*)				
12	1302 (8)	1301 (12)		1303 (10 *d*)	1320 (6)	CH_2 Wagging and
13	1330 (16)	1327 (15)	1322 (10)	1321 (10 *d*)	1330 (10)	Twisting
			1339 (12)			
			1346 (12)			$O-NO_2$
14	1394 (6 *d*)	1396 (8 *d*)	1390 (10)	1375 (3 *d*)	1395 (2)	C–O stretch ?
15	1414 (20)	1412 (17)	1412 (10)	1414 (15)	1414 (6 *d*)	$-C\overset{O}{\underset{O}{<}}$ Valence
16	1453 (10)	1450 (8)	1443 (10)	1441 (12)	1441 (4 *s*)	CH_2 Scissoring
	1463 (4 *d*)	1460 (5)			1459 (4 *d*)	
			1497 (5)			
17	1507 (9)	1506 (10)	1512 (3)	1483 (6)	1506 (3 *d*)	NH_3^+deforma-
18	1599 (7)	1593 (8)	1584 (9)	1609 (10)	1563 (4 *d*)	tion
			1625 (5)			$O-NO_2$
19	1627 (4 *d*)	1610 (5 *d*)	1644 (5)	1648 (5)	1640 (1)	$-C\overset{O}{\underset{O}{<}}$ Valence
20	1671 (1)	1670 (1)	1675 (4)	1675 (10)	1668 (2)	C=O ionised carboxyl
	1900 (1 *d*)	1910 (0)				
	2030 (2 *d*)	2000 (2 *d*)				
21	2459			2528 (1 *d*)	2530 (1 *d*)	O...H...O
	2553 (2 *d*)					
22	2613 (4 *d*)	2592 (3 *d*)	2620 (2 *d*)	2651 (3 *d*)	2630 (3 *d*)	N–H hydrogen
			2642 (2 *d*)			bonded
23	2652 (4 *d*)	2702 (3 *d*)	2707 (3 *d*)			
		2724 (4 *d*)				
				2763 (4 *d*)	2750 (2 *d*)	do.
	2713 (3 *d*)	2785 (7 *d*)	2751 (3 *d*)			do.
24	2790 (4 *d*)	2874 (7 *d*)	2806 (3 *d*)	2874 (5 *d*)	2830 (2 *d*)	do.
25	2853 (5 *d*)	2907 (8 *d*)	2882 (4 *d*)	2930 (5 *d*)	2895 (2 *d*)	do.
		2917 (7 *d*)				
26	2974 (19)	2967 (16)	2966 (15)	2962 (13)	2974 (5 *d*)	CH stretch
	2994 (20)	2986 (20)		2988 (15)		do.
27	3006 (11)	3002 (13)	3002 (13)	3004	3008 (8)	do.
28	3040 (8)	3029 (5)	3039	3022 (13)		NH_3^+
	3066 (3 *d*)	3067 (4 *d*)				do.
29	3126 (7 *d*)	3122 (7 *d*)	3143 (2 *d*)	3150 (6 *d*)	3145 (3 *d*)	do.
30	3229 (2 *d*)	3221 (4 *d*)	3252 (2 *d*)	3230 (5 *d*)		do.
				3270 (4 *d*)		do.
			3339 (1 *d*)			

TABLE II

External frequencies

Diglycine hydrochloride	Diglycine hydrobromide	Diglycine nitrate	Triglycine sulphate	α-Glycine
37 (6)	36 (2)			
	49 (5)	42 (4)	45 (6)	53 (7)
60 (5)	65 (7)	60 (4)	63 (10)	
73 (11)			73 (10)	74 (6 *s*)
	86 (8)	88 (10)		90 (1)
101 (8)	97 (11)	105 (9)	102 (10)	109 (9)
116 (3)	108 (6)			
141 (6)	139 (5)	141 (6)	129 (5)	
	158 (7)	153 (13)		
171 (7)	169 (5)	168 (5 *d*)	171 (8)	164 (5 *s*)
191 (4)	187 (4)	186 (4 *d*)		183 (4 *s*)
203 (2 *d*)	207 (3)	211 (3 *d*)	220 (4 *d*)	199 (3 *s*)
221 (2 *d*)		250 (1 *d*)		

Fifty-one Raman lines in the case of G_2Cl, 52 in the case of G_2Br and 46 in the case of G_2N have been recorded in the present investigation. Of these 10 in the case of G_2Cl, 11 in the case of G_2Br and 10 in the case of G_2N belong to the lattice spectra. The diffuse Raman line at 2030 appearing in G_2Cl falls on a weak mercury line. The presence of this could be easily seen by a comparative study of the photograph as well as the microphotometer record.

Edsall (1936) and Takeda *et al.* (1958) have recorded the Raman spectrum of glycine hydrochloride in aqueous solution and have reported the following frequency shifts 503, 577, 657, 871, 912, 1043, 1120, 1259, 1316, 1433, 1516, 1630, 1743, 2974 and 3017. These lines have been recorded by the author in the spectrum of single crystals of G_2Cl except 1743 cm.$^{-1}$ the presence of which is unfortunately masked by the triplet with the λ 2536·5 excitation.

4. STRUCTURE DATA

G_2Cl crystallises in the orthorhombic class in the space-group $P2_1\,2_1\,2_1$. The crystal structure has been determined by Theodor Hahn and Buerger (1957). The unit cell has 4 molecules of diglycine hydrochloride, with $a = 8{\cdot}15$ Å, $b = 18{\cdot}03$ Å and $c = 5{\cdot}34$ Å. According to these authors, slabs of glycine molecules are extending perpendicular to *b*, and zig zag Cl-Cl chains are along a screw parallel to *c*. The Cl chains are bonded on both sides to two molecules by means of hydrogen and Van der Waals bonds. The main effect of this

chain is to orient the molecules in such a way as to turn their NH_3 groups towards Cl forming N....Cl hydrogen bonds. In the glycine molecules, strong forces are effective between the molecules, particularly the strong O....O and N....O hydrogen bonds. The chemical formula for G_3Cl is $(NH_3\,CH_2.C\bar{O}\bar{O}).(NH_2\,CH_2.COOH)Cl$.

G_2Br also crys allises in the orthorhombic symmetry in the space-group $P2_1\,2_1\,2_1$. The cell dimensions are: $a = 8{\cdot}21$ Å, $b = 18{\cdot}42$ Å and $c = 5{\cdot}40$ Å. The unit cell consists of 4 mol ecules of diglycine hydrobromide. The crystal structure was determined by Theodor Hahn, El a Barney and M. J. Buerger (1956). Its chemical formula is similar to that of G_2Cl.

At room temperature G_2N crystallises in the monoclinic class, space-group $P2_1/a$ with $a = 9{\cdot}496$ Å, $b = 5{\cdot}107$ Å, $c = 9{\cdot}35$ Å and $\beta = 98{\cdot}8°$. The unit cell has 2 molecules of diglycine nitrate. The nitrate groups must be disordered or rotating in the room temperature phase, since the N-atoms of the nitrate groups are occupying the centres of symmetry. It goes into the ferroelectric phase below − 67° C. The transition to the ferroelectric phase is of second order type (Pepinsky, Vedam, Okaya, 1958).

5. Discussion

(i) *Internal Frequencies*

As is to be expected, there is a close correspondence between the frequency shifts observed in the various addition compounds of glycine. The common frequency shifts have been serially numb red in column 1. From a comparison of the frequency shifts observed in the Raman spectra of these compounds and those observed in similar organic compounds, the assignments for these common frequencies have been indi ated in the appropriate column in Table II The common frequency shifts numbered 10, 11, 16, 17, 18, 19, 21 and 22 exhibit appreciable variations from compound to compound. This may be attributed to the influence of the hydrogen bonds of different strengths in different compounds. The vibrations $-C\bar{O}\bar{O}$ rocking (3), $-C\bar{O}\bar{O}$ wagging (4) and CH_2 scissoring (16) are found to be split up and give rise to two frequencies each in G_2Cl and G_2Br. The CH_2 scissoring vibrations in G spectrum and NH_3 deformation (17) in G_2N are also found to split up. The splitting of the above lines may be due to the following: (i) larger number of molecules in the unit cell, and (ii) the effect of crystalline field. The CH stretching vibration appear s as 3 lines in G_2Cl, G_2Br and G_3S, whereas only two lines are observed in G and G_2N. It should be mentioned that combination of any two intense lines in the region 1300–1600 will fall in the region of CH stretching vibrations. This might partly explain the intense background in this region,

or it may also be due to O...H...O oscillations. A series of discrete lines appear in the region (apart from the background) 2900–3270 cm.$^{-1}$ in all the above crystals. These frequencies may be due to N–H oscillations arising from zwitterion structure of the glycine group and N...H...O (hydrogen, bonded) oscillations. In the case of G_2Cl and G_2Br the N–H...Cl or N–H...Br oscillations can appear in this region for the bond distances observed in these crystals (Nakamato, 1955; Pimental, 1956; Lord and Merrifield, 1953). In the region 2600–2950 cm.$^{-1}$ a series of well-defined broad and intense lines are observed in the spectra of glycine and its addition compounds. These are assigned as N–H hydrogen bonded stretching vibration. A faint band at about 2500 is observed in the case of G_2Cl spectrum. A band in the same region can also be seen with some difficulty in the spectra of G_2Br and G_2N although they have not been marked in the microphotometer. This may be attributed to O...H...O hydrogen bonds of very short distances.

The Raman lines 1900 and 2030 in G_2Cl and the corresponding lines at 1910 and 2000 in G_2Br appear to be peculiar to the halide addition compounds. In this connection, it is worthwhile to point out that in the case of NH_4Cl and NH_4Br, Krishnan (1947–48) observed frequency shifts at about 2000 cm.$^{-1}$ He was unable to explain satisfactorily the existence of this line. In the case of glycine halides two more lines are observed in the region 1250. The diffuse lines around 1250 cm.$^{-1}$ may be due to C–OH vibrations. Similar bands are also observed in the infra-red spectra of amino-acid hydrohalides by Randall (1949), Josien *et al.*, in amino-acids (1951), and Flett (1951) and Ananthanarayanan (1960) in the Raman spectra of dicarboxylic acids.

The principal frequency shifts of HCl acid and HBr acid are at about 2760 cm.$^{-1}$ and 2465 cm.$^{-1}$ respectively. A corresponding frequency may not appear in G_2Cl and G_2Br because of the presence of N–H...Cl and N–H...Br hydrogen bonds.

NO_3^- ion.—If the nitrate ion has the symmetry D_{3h}, it is expected to give rise to frequencies 1050 (totally symmetric oscillation observed as a very intense line), 720 and 1350 (doubly degenerate oscillations) and 830 (Theimer, 1950). The frequency 1053 observed in G_2N may correspond to 1036 line observed in all the other compounds both from the intensity point of view as well as the sharpness. Also in the spectrum one do not observe any line corresponding to 720 cm.$^{-1}$ If the NO_3 ion is of the form $O–NO_2$ as in the case of alkyl nitrates it may give rise to frequencies in the region 1640–1628, 1285–1260 cm.$^{-1}$ (symmetrical) and ester deformation vibration near 610–560 cm.$^{-1}$ (West, 1956; Nibben, 1939). The spectrum of G_2N exhibits two feeble lines 540, 561, two very intense and broad lines 1339 and 1346 and a line of

moderate intensity at 1625 cm.$^{-1}$ These are not recorded in the spectra of the other addition compounds. This observation seems to support the view of staggered configuration for NO_3 ion in G_2N. Fairly big crystals are being grown to undertake the orientation and polarisation work which could give some more information regarding the nature of the NO_3 ion.

The complete X-ray structure analysis should confirm the staggered configuration for NO_3 ion.

(*ii*) *Lattice Spectrum*

G_2Cl, G_2Br and G_2N exhibit nearly the same number of low frequency lines. There seems to be a close correspondence between the frequencies of G_2Br and G_2N, the only difference being in the G_2Br spectrum the lines are sharp, whereas in the G_2N spectrum the lines are broad. This is indeed surprising in view of the fact that both have got different crystal structures.

In the case of G_2Cl, G_2Br, one can work out group theoretically the number of lines that are allowed to appear in Raman effect for the space-group $P2_1\,2_1\,2_1$ taking the whole molecule as one unit. Nine translatory and 12 rotatory modes should be active in Raman effect. In organic crystals the oscillations of rotatory type are expected to appear more strongly. Actually 10 lines are observed in G_2Cl and 11 lines in G_2Br and these should be attributed to rotatory type of oscillations.

On the same basis in the case of G_2N only 6 rotational modes are permitted in Raman effect (space-group $P2_{1/a}$). Actually one observes 10 frequency shifts. Taking the 2 glycines as 2 units and nitrate as the third unit, one finds that 6 translatory and 12 rotatory modes should be active in Raman effect. If the translatory modes as usual are of negligible intensity, twelve rotational modes will appear with appreciable intensity in the lattice spectrum.

6. Summary

Raman spectra of single crystals of diglycine hydrochloride, diglycine hydrobromide and diglycine nitrate have been recorded for the first time. λ 2536·5 resonance radiation of mercury has been used as exciter. The spectrum of diglycine hydrochloride exhibits 10 low frequency lines and 41 lines due to internal oscillations, while that of diglycine hydrobromide exhibits 11 lines and 41 lines respectively. In the case of diglycine nitrate 46 lines have been recorded, of which 10 belong to the lattice spectrum. These spectra are compared with the Raman spectra of triglycine sulphate and α-glycine and proper assignments have been given to the internal oscillations.

7. ACKNOWLEDGEMENT

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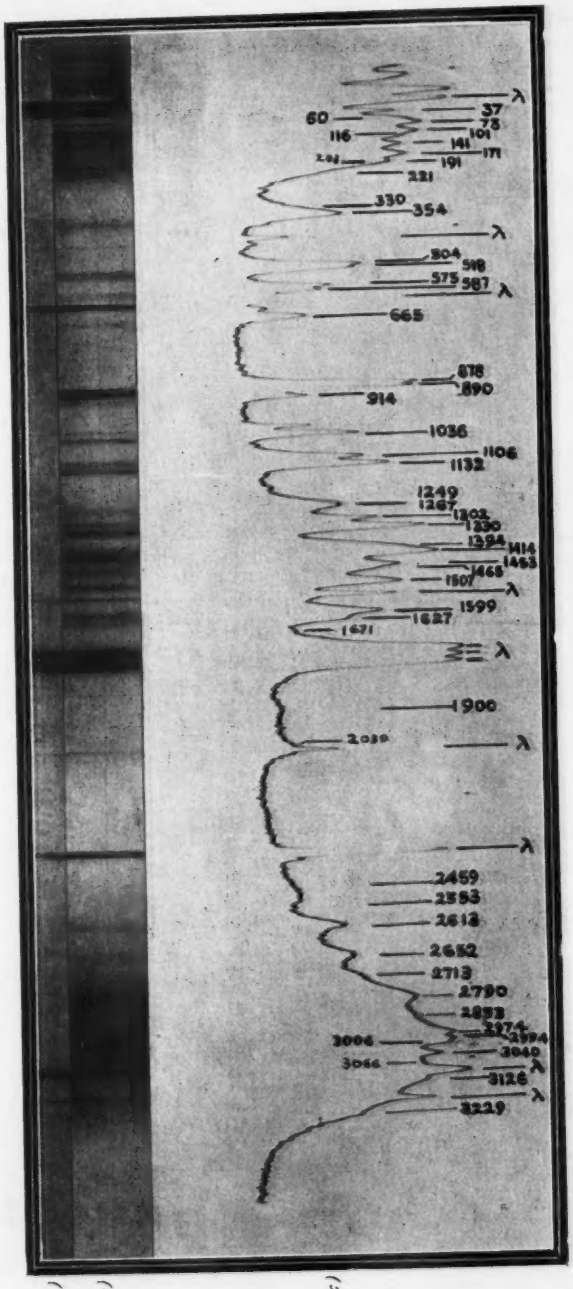

FIG. 1

(a) Mercury Spectrum.
(b) Raman Spectrum of Diglycine Hydrochloride.
(c) Microphotometer Record.

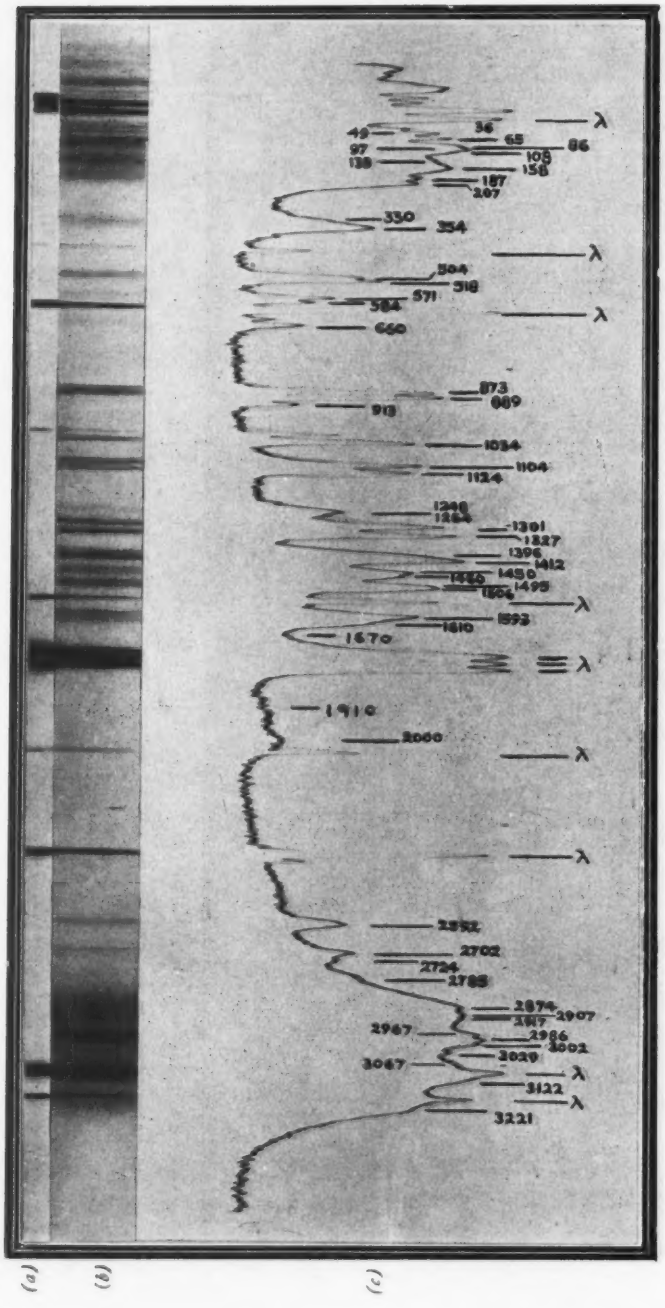

FIG. 2

(a) Mercury Spectrum.
(b) Raman Spectrum of Diglycine Hydrobromide.
(c) Microphotometer Record.

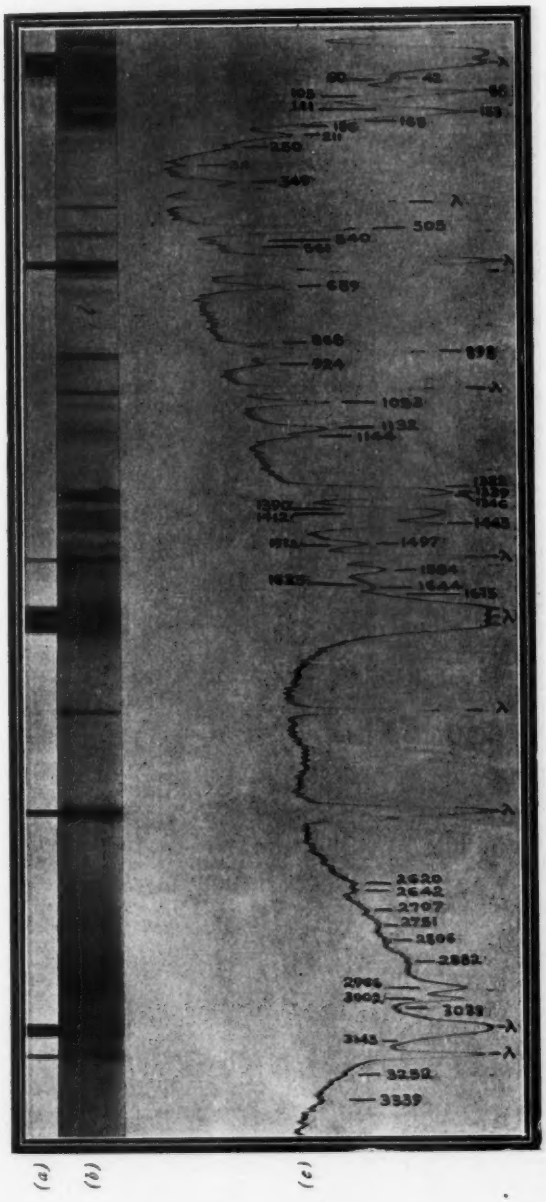

FIG. 3

(a) Mercury Spectrum.
(b) Raman Spectrum of Diglycine Nitrate.
(c) Microphotometer Record.

SYNTHESIS OF THE LACTONE OF 2-CARBOXY-4-HYDROXY-7-METHOXY-1, 2, 3, 4-TETRAHYDROPHENANTHRONE

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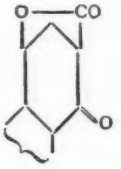
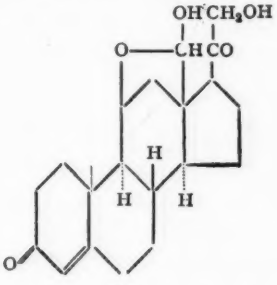
The high physiological activity of aldosterone prompted us to undertake the investigation on the synthesis of its analogues where the hydrindane system was fused with aromatic nuclei. These might be expected to have interesting physiological properties in view of Simpson and Tait's[1] observation that in its high biological potency and low concentration in biological fluids aldosterone resembles the oestrogens rather than the adrenal hormones.

For these analogues it was considered desirable to build the five-membered ring on compounds with the partial structure (I) possessing a β-keto-



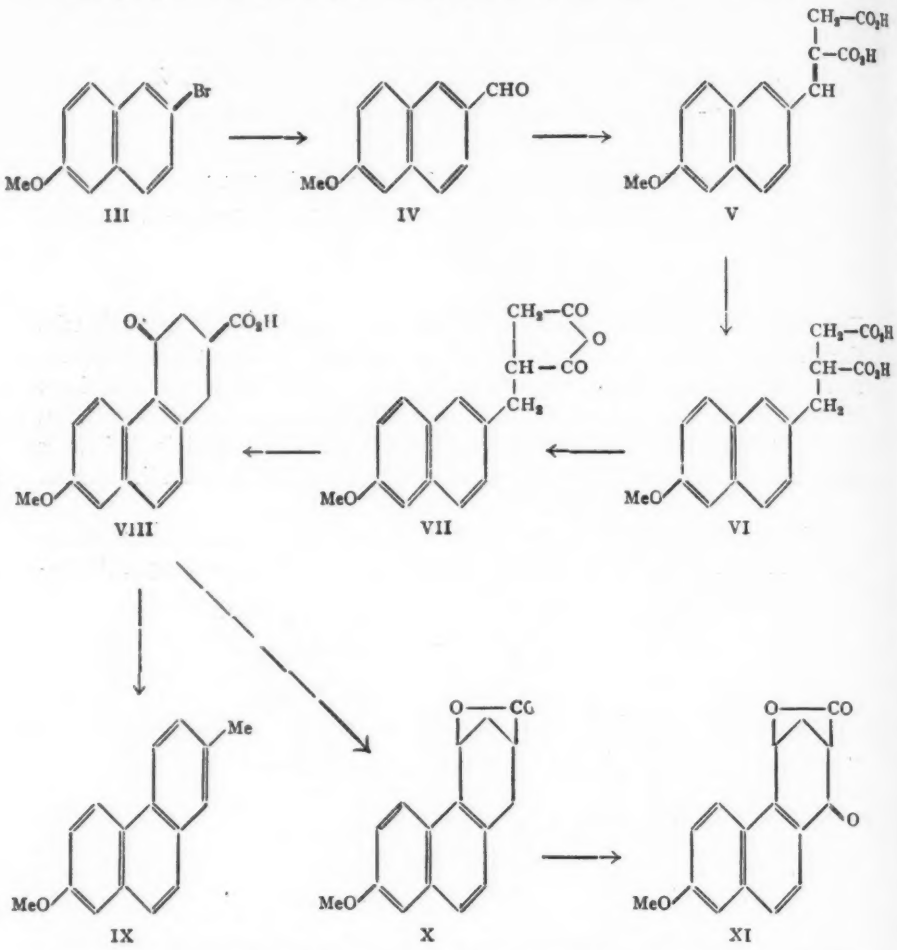
I



II

lactone group which might be easily convertible to the hemi-acetal group of aldosterone (II) at a later stage, after formation of the D-ring. With this end in view the lactone of 2-carboxy-4-hydroxy-6-methoxytetralone (XII) was prepared and reported in an earlier paper.[2] The present paper deals with the synthesis of the lactone of 2-carboxy-4-hydroxy-7-methoxy-1, 2, 3, 4-tetrahydrophenanthrone (XI) starting from 6-methoxynaphthaldehyde-2 (IV).

6-Methoxynaphthaldehyde-2 (IV) was prepared by the method of Tard,



Lapin and Horeau,[3] which consisted of the condensation of the Grignard reagent prepared from 2-bromo-6-methoxynaphthalene (III) in tetrahydrofuran[4, 5] with dimethyl formamide. Another method employed by us was to condense 2-lithium-6-methoxynaphthalene[3] with dimethyl formamide in ether without impairing the yield.

The Stobbe condensation of the aldehyde (IV) with dimethyl succinate in refluxing methanolic sodium methoxide followed by *in situ* hydrolysis of

the half-ester furnished γ-(6-methoxy-2-naphthyl)-itaconic acid (V). Reduction of an alkaline solution of the unsaturated diacid (V) with nickel aluminium alloy[7] at 90° yielded γ-(6-methoxy-2-naphthyl)-β-carboxybutyric acid (VI), the equivalent weight and analytical data indicated that the methoxyl group was not eliminated, as was observed in a few instances of similar reductions.[8] Treatment of the diacid (VI) with acetyl chloride yielded the anhydride (VII).

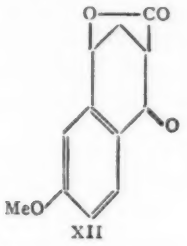
Friedel-Crafts cyclisation of the anhydride (VII) could theoretically yield the following four compounds: (i) 2-carboxy-7-methoxy-4-oxo-1, 2, 3, 4-tetrahydrophenanthrene (VIII); (ii) 3-carboxy-6-methoxy-1-oxo-1, 2, 3, 4-tetrahydroanthracene; (iii) 6, 7-(5′-methoxybenzo)-indanone-2-acetic acid; (iv) 5, 6-(5′-methoxybenzo)-indanone-2-acetic acid. It is known that the angularly-fused ring-formation is preferred to the linear one and that Friedel-Crafts cyclisation yields six-membered rings in preference to five-membered ones,[9] therefore, it was hoped that the phenanthroic acid (VIII) would be the major product. The reaction yielded a solid which after a single crystallisation melted at 217°. The ultra-violet absorption maxima at 245·5 mμ log ε 4·59, 310·5 mμ log ε 3·88 and 350 mμ log ε 3·57 have close resemblance to those reported for 3-methoxy-11-oxoequilenane by Newman *et al.*[6] The carbonyl region of the infra-red spectrum (in Nujol) showed two peaks at 1665 cm.$^{-1}$ (conjugated cyclohexane carbonyl) and 1705 cm.$^{-1}$ (acid dimer); a conjugated cyclopentane carbonyl and the acid dimer peaks might be expected to overlap.

Chemical proof in favour of the phenanthrene structure for the compound obtained by cyclisation of the anhydride (VII) was provided as follows. The keto-acid was treated with lithium aluminium hydride, and the crude diol on dehydration with potassium hydrogen sulphate followed by dehydrogenation with 30% palladium on charcoal yielded 7-methoxy-2-methylphenanthrene (IX).[10]

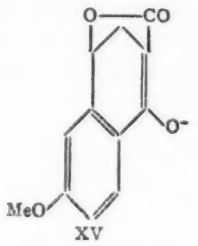
Reduction of a neutral aqueous solution of the sodium salt of 2-carboxy-7-methoxy-1, 2, 3, 4-tetrahydrophenanthrone-4 (VIII) with sodium borohydride afforded the lactone (X). Oxidation of the lactone (X) with chromium trioxide in acetic acid yielded the lactone of 2-carboxy-4-hydroxy-7-methoxy-1, 2, 3, 4-tetrahydrophenanthrone (XI).

We next investigated the alkylation of the β-keto-lactone system (I) in order to form the D-ring. Condensations of the keto-lactone (XII)[2] with diethylaminobutan-2-one methoiodide in the presence of sodium hydride

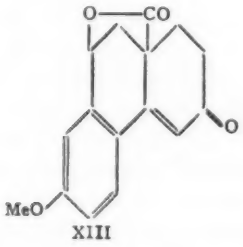
or potassium in benzene and with methallyl chloride in the presence of potassium carbonate and potassium iodide[11] resulted in the recovery of the keto-lactone (XII). Condensation with methyl vinyl ketone in the presence of



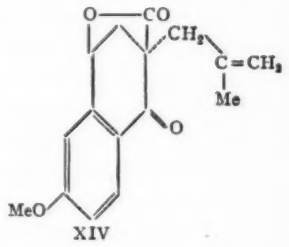
XII



XV



XIII



XIV

"Triton B"[12] or with diethylamino-butan-2-one methoiodide with sodium hydride in pyridine did yield a small quantity of a chromatographed fraction having the anticipated ultra-violet peak at 323 mμ (for the structure XIII), but the materials were extremely impure (ε *ca.* 500). When the potassio-derivative of the keto-lactone (XII), prepared by treating the keto-lactone (XII) with potassium *t*-butoxide and then completely removing the *t*-butanol under anhydrous conditions,[13] was treated with methallyl chloride in acetone, a small quantity of a material with ultra-violet peaks at 224·5 mμ log ε 4·01 and 277 mμ log ε 3·94, presumably (XIV), was obtained on repeated chromatography of the reaction product.

Presumably, the reason for the failure of alkylation of the keto-lactone (XII) is that the formation of the enolate ion (XV) constitutes the violation of Bredt's rule.[14, 15, 16]

EXPERIMENTAL

6-*Methoxynaphthaldehyde*-2 (*IV*).—To a vigorously stirred and cooled (ice and salt) solution of dry 2-bromo-6-methoxynaphthalene (III) (12·0 g.) in anhydrous benzene (75 ml.) under a stream of nitrogen was added an ethereal solution of *n*-butyllithium[17] (from 1·08 g. of lithium and 8·56 g. of *n*-butyl

bromide and 100 ml. of ether) over a period of 5 min. After stirring the reaction mixture for a further 20 min. at — 5°, a solution of dimethyl formamide (4·4 g.) in dry benzene (5 ml.) was added slowly within 5 min. The pale green reaction mixture was left under the nitrogen atmosphere for 2 hours at 0° and then slowly raised to room temperature overnight. The reaction mixture was decomposed (0°) with aqueous ammonium chloride. The organic phase was separated and the aqueous phase extracted with ether. The combined organic phase was washed with water and dried, and the solvent was removed. The crude residue was crystallised from ether-light petroleum (40–60°) to yield 6-methoxy-naphthaldehyde-2 (IV) (5·9 g.) m.p. 74–79°. It was recrystallised from benzene-hexane, m.p. 81° (reported[3] 79°); U.V.: $\lambda_{max.}^{ale.}$ 243 mμ log ε 4·56, 248 mμ log ε 4·56, 261 mμ log ε 4·44 and 310–12 mμ log ε 4·20 (Found: C, 77·2; H, 5·5. Calc. for $C_{12}H_{10}O_2$. C, 77·4; H, 5·4%).

γ-(6-Methoxy-2-naphthyl)-itaconic Acid (*V*).—To a vigorously stirred refluxing solution of methanolic sodium methoxide, prepared from sodium (1·92 g.) and methanol (20 ml.), was cautiously added a solution of the naphthaldehyde (IV) (6·2 g.) and freshly distilled dimethyl succinate (5·35 g.) in methanol (50 ml.) and benzene (10 ml.). The stirring and refluxing were continued for 2·5 hours, then water (100 ml.) was added cautiously (considerable bumping occurs due to the separation of solid) with simultaneous distillation of the methanol. When the methanol had ceased to distil, the contents were cooled and added to water (100 ml.). The aqueous solution of the sodium salt was washed with ether and then run into an excess of cold 6N-hydrochloric acid. The pale yellow precipitate (5·43 g.), m.p. 175–185° d., was crystallised from aqueous alcohol (norit). The *itaconic acid* (V) melted at 196–197° d.; U.V.: $\lambda_{max.}^{alc.}$ 220 mμ log ε 4·50, 263 mμ log ε 4·52 and 301 mμ log ε 4·26 (Found: C, 66·8; H, 5·1%; eq. wt. 146·3. $C_{16}H_{14}O_5$ requires C, 67·2; H, 4·9%; eq. wt. 143·1).

γ-(6-Methoxy-2-naphthyl)-β-carboxybutyric Acid (*VI*).—To a well-stirred solution of the unsaturated diacid (V) (3·6 g.) in 10% aqueous sodium hydroxide (100 ml.), kept at 92–93°, was added a few drops of octyl alcohol and then, in small portions, 1 : 1-nickel-aluminium alloy (10 g.) over a period of 25 min. The stirring was continued for 1 hour at 95°, and then the hot material was filtered carefully under suction, the catalyst being washed well with hot water. The warm filtrate was slowly run into concentrated hydrochloric acid (300 ml.) with efficient stirring. The milky solution deposited a white precipitate (2·35 g.), m.p. 168–170°. *γ-(6-methoxy-2-naphthyl)-β-carboxybutyric acid* (*VI*) was crystallised from aqueous alcohol, m.p. 170–71°;

U.V.: $\lambda_{max.}^{alc.}$ 227 mμ log ε 4·79, 262 mμ log ε 3·75, 272 mμ log ε 3·75, 318 mμ log ε 3·27 and 332 mμ log ε 3·35 (Found: C, 66·7; H, 5 4%; eq. wt. 145·3. $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%; eq. wt. 144·1).

Anhydride of γ-(6-Methoxy-2-naphthyl)-β-carboxybutyric Acid (*VII*).—To the diacid (VI) (2·20 g.) was added an excess of acetyl chloride (50 ml.); the flask became cold during the dissolution of the acid and a clear pale yellow solution was obtained. After 6 hours at room temperature, the acetyl chloride was completely removed, and the residue (2·00 g.), m.p. 139–40°, was crystallised from dry benzene-light petroleum (40–60°) to yield the *anhydride of γ-(6-methoxy-2-naphthyl)-β-carboxybutyric acid* (*VII*), m.p. 140° (Found: C, 70·8; H, 5·1% $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%).

2-*Carboxy-7-methoxy*-1, 2, 3, 4-*tetrahydrophenanthrone*-4 (*VIII*).—A solution of the anhydride (VII) (1·87 g.) in nitrobenzene (50 ml.) was run into a well-stirred solution of aluminium chloride (2·7 g.) in nitrobenzene (20 ml.) at room temperature (23°). After stirring overnight the product was decomposed with ice and hydrochloric acid. After removal of the nitrobenzene by steam-distillation, a solid (1·84 g.), m.p. 200–10°, was isolated by filtration of the cooled mixture. 2-*Carboxy-7-methoxy*-1, 2, 3, 4-*tetrahydrophenanthrone*-4 (*VIII*) was crystallised from aqueous alcohol (norit), m p. 217°; U.V.: $\lambda_{max.}^{alc.}$ 245·5 mμ log ε 4·59, 310·5 mμ log ε 3·88 and 350 mμ log ε 3·57; I.R. (Nujol): 3·39 μ (hydroxyl), 5·87 μ (acid dimer), 6·01 μ (conjugated cyclohexane carbonyl) (Found: C, 70·8; H, 5·1%; eq. wt. 269·7. $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%; eq. wt. 270·3).

Conversion of 2-*Carboxy-7-methoxy*-1, 2 3, 4-*tetrahydrophenanthrone*-4 (*VIII*) *into* 7-*Methoxy-2-methylphenanthrene* (*IX*).—A solution of the keto-acid (VIII) (0·5 g.) in tetrahydrofuran (75 ml.) was added slowly with swirling to lithium aluminium hydride (0·15 g.) in tetrahydrofuran (100 ml.). After standing the mixture for 1 hour at room temperature, it was refluxed for 2 hours. It was then decomposed at 0° by cautious addition of a little water followed by cold 10% sulphuric acid (20 ml.). The mixture was poured into water and repeatedly extracted with ether. The ethereal extract was washed successively with cold potassium carbonate solution and brine, and then dried. After removal of the solvent, the neutral viscous residue (0·18 g.) was heated with freshly fused potassium bisulphate (2 g.) at 170–175° in an atmosphere of nitrogen. The dehydrated product (0·094 g.), isolated by short-path distillation at 150–60° (bath)/1 mm., was dehydrogenated in a Heymann's apparatus with 30% palladium on carbon (100 mg.) under a stream of carbon dioxide at 310–30° for 2·5 hours. The sublimate (0·04 g.), m.p. 130–40°,

was crystallised as described by Bachmann and Chemerda,[10] when 7-methoxy-2-methylphenanthrene (8 mg.), m.p. 142–43° (reported[10] 144·5–45·5°), was obtained (Found: C, 86·2; H, 6·2%. $C_{16}H_{14}O$ requires C, 86·5; H, 6·4%).

Lactone of 2-*Carboxy*-4-*hydroxy*-7-*methoxy*-1, 2, 3, 4-*tetrahydrophenanthrene* (*X*).—Sodium borohydride (0·50 g.) was added to a solution of the keto-acid (VIII) (4·50 g.) in 1 N-sodium hydroxide (16·7 ml.), and the contents were allowed to stand overnight at room temperature (23°). Dilute suphuric acid (5·1 ml. of concentrated acid in 100 ml. of water) was added and the contents heated for 15 min. on a boiling water-bath. It was cooled and poured into a large quantity of ether (*ca.* 1 l.) and the aqueous phase separated. The ether solution was washed with cold sodium bicarbonate solution and brine, and then dried. After removal of the solvent, the white waxy material (0·38 g.) was repeatedly triturated with hexane containing a trace of benzene. After removal of the liquid portion, the *lactone of* 2-*carboxy*-4-*hydroxy*-7-*methoxy*-1, 2, 3, 4-*tetrahydrophenanthrene* (*X*) was left as a white waxy solid, m.p. 48–51°; U.V.: $\lambda_{max.}^{alc.}$ 234 mμ log ε 4·74, 263 mμ log ε 3·76, 319 mμ log ε 3·28 and 334 mμ log ε 3·32; I.R. ($CHCl_3$): 5·66 μ (γ-lactone) (Found: C, 75·5; H, 5·7%. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·6%).

Lactone of 2-*Carboxy*-4-*hydroxy*-7-*methoxy*-1, 2, 3, 4-*tetrahydrophenanthrone* (*XI*).—To a solution of the lactone (X) (0·24 g.) in glacial acetic acid (2·1 ml.) and propionic acid (0·4 ml.), kept at 0°, was added a solution of chromium trioxide (0·2 g.) in water (0·2 ml.) and acetic acid (1·1 ml.) over a period of 7 min. It was kept for 40 min. at 0° and overnight at room temperature. After destroying any excess oxidising mixture with a little methanol, the contents were poured into water (50 ml.) and extracted with ether. The ether extract was washed with cold potassium carbonate solution and brine, and then dried (Na_2SO_4). After removal of the solvent, the white waxy residue was triturated with light petroleum (40–60°), when an amorphous powder (0·08 g.), m.p. 62–67°, was obtained. Crystallisation from ether-light petroleum (40–60°) yielded the *lactone of* 2-*carboxy*-4-*hydroxy*-7-*methoxy*-1, 2, 3, 4-*tetrahydrophenanthrone* (*XI*), m.p. 66–69°; U.V.: $\lambda_{max.}^{alc.}$ 254 mμ log ε 4·56, 265·5 mμ log ε 4·56, 290 mμ log ε 3·99, 301 mμ log ε 4·06 and inflexions at 245 mμ log ε 4·48, 282 mμ log ε 4·40 and 312 mμ log ε 3·92; I.R. ($CHCl_3$): 5·62 μ (γ-lactone), 5·98 μ (conjugated cyclohexane carbonyl) (Found: C, 71·2; H, 4·7%. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%).

Alkylation Experiments with the Keto-lactone (*XII*)

(*a*) *Using Methallyl Chloride in the presence of Potassium Carbonate and Potassium Iodide.*[11]—To a stirred mixture of the keto-lactone (XII) (1·09 g.)

dry potassium iodide (1·0 g.), freshly prepared potassium carbonate (1·36 g.) and anhydrous acetone (40 ml.) under a dry nitrogen atmosphere was added freshly distilled methallyl chloride (10 ml.) in five lots over 72 hours at room temperature. The reaction product was cocentrated in vacuum, water (100 ml.) was added, and the product extracted with ether (3×100 ml.). The ether solution was washed with brine and dried (Na_2SO_4), and the solvent was removed. The solid residue (1·0 g.) melted at 134–36° and was identified as the starting keto-lactone (XII).

(*b*) *Using Methallyl Chloride in the presence of Potassium t-Butoxide.*[13]—A solution of the keto-lactone (XII) (1·09 g.) in *t*-butanol (10 ml.) was added to a stirred solution of potassium *t*-butoxide, from potassium (0·21 g.) and *t*-butanol (20 ml.), under an atmosphere of nitrogen. The suspension was stirred overnight at room temperature and then made completely free from solvent under suction. To the residue, kept under nitrogen, was added dry acetone (50 ml.), anhydrous potassium iodide (1 g.) and methallyl chloride (3·2 g.) in acetone (30 ml.). After 50 hours at room temperature, the acetone was removed under reduced pressure, water (50 ml.) was added and the material extracted with ether. The ether solution was washed with sodium thiosulphate solution and brine, and then dried (Na_2SO_4). After removal of the solvent, the crude material (1·1 g.) was chromatographed over acid-washed alumina (30 g.) when a fraction (0·17 g.) showing ultra-violet absorption maximum at 224 mμ and 277 mμ was obtained in the benzene eluates. Short-path distillation, 100° (bath)/0·005 mm., and rechromatography over acid-washed alumina yielded the *lactone of 2-carboxy-4-hydroxy-2-methallyl-6-methoxytetralone* (*XIV*); U.V.: $\lambda_{max.}^{alc.}$ 224·5 mμ log ε 4·01 and 277 mμ log ε 3·94 (Found: C, 70·8; H, 6·3.% $C_{15}H_{18}O_4$ requires C, 70·6; H, 5·9%).

(*c*) *Using Diethylaminobutan-2-one Methoiodide in the presence of Potassium.*—A solution of the keto-lactone (XII) (1·1 g.) in benzene (30 ml.) was added in 5 min. to a suspension of potassium dust (0·20 g.) in benzene (10 ml.) in an atmosphere of nitrogen. The contents were refluxed for 8 hours and to the cooled (0°) material diethylaminobutan-2-one methoiodide[18] (1·70 g.) in pyridine (8 ml.) was added. After 3 hours at room temperature and 14 hours under reflux, the product was decomposed with 6 N-hydrochloric acid (50 ml.). The material was extracted with ether, and after washing the organic phase with sodium bicarbonate solution and brine, the solvent was removed. The gummy residue (0·85 g.) on crystallisation from benzene-light petroleum (40–60°) yielded the starting keto-lactone (XII), m.p. and mixed m.p. 136–37°.

(*d*) *Using Diethylaminobutan-2-one Methoiodide in the presence of Sodium Hydride in Benzene.*—A solution of the keto-lactone (XII) (0·55 g.) in benzene

(35 ml.) was added to a suspension of sodium hydride (0·12 g.) in benzene (30 ml.) under nitrogen. After refluxing for 4 hours, to the cooled contents was added diethylaminobutan-2-one methiodide[13] (0·84 g.) in pyridine (8 ml.), and after stirring the mixture for 8 hours at room temperature, it was kept under reflux for 5 hours. The reaction product was decomposed and worked up as usual, when the starting keto-lactone (XII) (0·35 g.), m.p. 135–36°, was obtained.

(*e*) *Using Diethylaminobutan-2-one Methiodide in the presence of Sodium Hydride in Pyridine.*—A solution of the keto-lactone (XII) (0·90 g.) in pyridine (35 ml.), and sodium hydride (0·12 g.) was stirred for 18 hours under nitrogen at room temperature (26–28°). The contents were cooled (0°) and diethylaminobutan-2-one methiodide[13] (1·40 g.) in pyridine (10 ml.) was added. After leaving the mixture for 3 hours in an ice-bath and overnight at room temperature, dry ether (100 ml.) was added and the contents gently refluxed for 1 hour. It was cooled, dry ether (100 ml.) was added, and the contents were poured with stirring into crushed ice (500 g.) and hydrochloric acid (100 ml.). The ether layer was separated and the aqueous layer extracted with ether. The combined ether solution was washed successively with water-sodium bicarbonate solution and brine. After drying (Na_2SO_4), the solvent was removed and the residue (0·70 g.) on short-path distillation at 150–70° (bath)/0·005 mm. yielded a viscous material (0·50 g.). Chromatography of the distillate over acid-washed alumina (15 g.) yielded in the 1 : 1 benzene-light petroleum (40–60°) eluates a material having ultra-violet absorption maxima at 322 mμ log ε 2·81 and 336 mμ log ε 2·42 (log ε calc. for XIII).

(*f*) *Using Methyl Vinyl Ketone in the presence of "Triton B".*[12]—To a solution of the keto-lactone (XII) (0·55 g.) in absolute ethanol (5 ml.) was added 37% methanolic "Triton B" (1·3 ml.) and 85% methyl vinyl ketone (0·65 ml.), and the contents were refluxed for 2 hours on a steam-bath. It was cooled to 0°, 3 N-hydrochloric acid (2 ml.) was added and the mixture then heated for 30 min. on a steam-bath. The contents were concentrated under reduced pressure and then worked up as usual. Chromatography of the crude residue (0·42 g.), obtained after removal of the solvent, on acid-washed alumina (14 g.), yielded in the alcohol eluates a material (0·08 g.) having ultra-violet absorption maximum at 322–24 mμ log ε 3·1 (log ε calc. for XIII).

Summary

Starting from 6-methoxynaphthaldehyde-2, 2-carboxy-7-methoxy-1, 2, 3, 4-tetrahydrophenanthrone-4 was prepared. Sodium borohydride reduction of the keto-acid followed by chromic acid oxidation yielded the lactone of

2-carboxy-4-hydroxy-7-methoxy-1, 2, 3, 4-tetrahydrophenanthrone. Alkylation of the lactone of 2-carboxy-4-hydroxy-6-methoxytetralone was not promising.

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